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NEQPAK, The AEDC Thermochemical Nonequilibrium Package- Theory and Use

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Calspan Corporation/AEDC Operations

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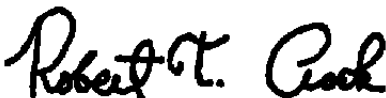
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13. ABSTRACT (Maximum 200 words) NEQPAK is a set of Fortran 77 routines and databases which are useful in the development and application of nonequilibrium flow solvers. The set includes a library of subroutines for evaluating reaction rates and the thermal and transport properties of high-temperature ionized gases. Thermal nonequilibrium may be treated by applying modules which evaluate the interactions between molecular energy modes. The interactions between vibrational and chemical relaxation may be investigated by using multiple-temperature reaction models or by applying the coupling factors suggested by contemporary theories. A utility for correlating user-supplied reaction data with the material properties database is also provided. Most of the modules are optimized for use on vector-processing machines, and have been designed for the efficient use of memory. The thermal properties database covers the range from 100 to 35,000 K, and the transport properties database extends from 300 to 30,000 K. This report describes the thermophysical models embodied in NEQPAK and explains how the routines may be incorporated into hypersonic CFD codes.				
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PREFACE

The work reported herein was performed by the Arnold Engineering Development Center (AEDC), Air Force Materiel Command (AFMC) under Program Element 65807F, Control Number 9R02, AEDC Project Number 0118, at the request of the AEDC Technology Division (AEDC/DOT). The Air Force Project Manager was Capt. S. G. Tennent.

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1.0 INTRODUCTION

The analysis of flow fields associated with hypersonic and other types of reacting flows has provided the impetus for the development of computational methods applicable to nonequilibrium flow fields. Flows of this nature are often associated with hypersonic aircraft, planetary reentry vehicles, arc heaters, and propulsion systems. As Tirskey (Ref. 1) has pointed out, the flow fields associated with certain hypersonic configurations (e.g., reentry vehicles) experience both chemical and thermal nonequilibrium. Numerical simulations of chemically and thermally relaxing flows require the input of large amounts of property data and of assumed relaxation models (e.g., reaction rates) which must then be manipulated into a form which is accessible to a flow solver. While these data are available for most of the materials of concern at the AEDC, they are widely scattered and often are presented in different dimensional units and unfamiliar forms. Comparing the results of codes which assume different material properties and relaxation models is nearly impossible. As a result, the assembly of diverse nonequilibrium data and thermochemical models into a single package with a common format is an essential part of the computational fluid dynamics (CFD) effort at the AEDC.

Since the use of such a common database fixes most of the input formats for the user code and essentially determines the methods for calculating transport and thermal properties, efficient routines for performing these functions can be prepared in advance and associated with the database in a "chemistry package." Furthermore, since there is virtual unanimity on the functional form of the reaction rate — at least for elementary reactions — this package can also contain a subroutine for evaluating the source terms in the species conservation and energy conservation equations.

A number of such "chemistry packages" (Refs. 2-4) is available. The particular package, NEQPAK, described in this report is unique because it allows for thermal nonequilibrium, for multiple-temperature reaction models, and for very high temperatures. NEQPAK consists of a database of reaction rates and molecular properties, and subroutines to evaluate the properties as required. In addition, there are subroutines to evaluate the source terms and their derivatives as well as utility routines to convert units and to compute some frequently used functions of the composition. In essence, NEQPAK provides the facilities needed to evaluate the right-hand sides of the reacting flow equations without limiting the choice of flow solver algorithms.

A preliminary version of NEQPAK has been incorporated into a one-dimensional flow solver (Ref. 5) which has been shown to compare very well with results obtained with other codes (Ref. 6).

The aerophysical models embedded in NEQPAK are discussed in Sec. 2.0. These models have been extended to include the effects of ambipolar diffusion and nonequilibrium thermal conductivity in Appendixes A and B. The extent and validity of the database are discussed in Sec. 2.7. An overall picture of NEQPAK and how it might fit into a typical CFD code may be obtained by following the "scenario" of Appendix I. Detailed information required for inclusion of NEQPAK routines into a flow solver is presented in Secs. 3.1-3.9. Recommendations for continuing the availability and utility of NEQPAK as a state-of-the-art tool are given in Sec. 4.0. The Fortran variables in common are listed in Appendix C. All NEQPAK modules are listed in Appendix D. Appendix E discusses the procedure for providing the reaction model input. Sample reaction input sets are listed in Appendix F. These reactions are not a part of NEQPAK *per se*, but are typical of the reaction data which the user must provide to any program which uses the NEQPAK package. Appendix G presents the material database format. The species for which data are currently available are listed in Appendix H.

2.0 AEROPHYSICAL MODELS

NEQPAK is designed to aid in the analysis of flow of a reacting mixture of perfect gases, i.e., gases which may be described by the thermal state equation,

$$p_s = \gamma_s \mathcal{R} T \quad (1)$$

where γ_s is the concentration of species s in $kg\text{-mole}/m^3$ and $\mathcal{R} = 8314.34 \text{ J}/kg\text{-mole}/K$ is the universal gas constant.* Dalton's law of partial pressures

$$p = \sum_{s=1}^{N_s} p_s \quad (2)$$

where N_s is the number of species, is also assumed. Equations (1) and (2) do not adequately describe the behavior of saturated vapors or of gases under very high pressures and low temperatures.

2.1 REACTING FLOW EQUATIONS

The equations which describe the flow of a reacting compressible gas may be derived from the principles of kinetic theory (Ref. 7). These equations provide for the conservation of species:

$$\frac{\partial \gamma_s}{\partial t} + \nabla_i (\gamma_s U^i) = -\nabla_i (\gamma_s u_s^i) + \dot{w}_s, \quad s = 1, \dots, N_s \quad (3)$$

* SI units are used throughout this report and in NEQPAK itself.

momentum:

$$\begin{aligned} \frac{\partial(\rho U^i)}{\partial t} + \nabla_j(\rho U^i U^j) = \\ -\nabla_i p + \nabla_j[\eta(\nabla_j U^i + \nabla_i U^j) - \frac{2}{3}\eta\delta_{ij}\nabla_k U^k] + \sum_{s=1}^{N_s} \gamma_s \mathcal{F}_s^i \quad i = 1, 2, 3 \end{aligned} \quad (4)$$

and energy:

$$\begin{aligned} \frac{\partial(\rho \hat{E})}{\partial t} + \nabla_i(\rho \hat{H} U^i) = \\ \nabla_j(\sum_{l=1}^{N_l} \lambda^l \nabla_j T_l) - \nabla_i(\sum_{s=1}^{N_s} \rho_s \hat{h}_s u_s^i) + \sum_{s=1}^{N_s} (U^i + u_s^i) \gamma_s \mathcal{F}_s^i \\ + \nabla_j[\eta U^i(\nabla_j U^i + \nabla_i U^j) - \frac{2}{3}\eta\delta_{ij} U^i \nabla_k U^k] - Q, \end{aligned} \quad (5)$$

where $\nabla_i = \partial/\partial x^i$ and the summation convention is employed. The concentration of species s is denoted by γ_s and the rate of change of concentration due to chemical reactions by $\dot{\omega}_s$ in conformity with the customary notation. Thermodynamic quantities such as the species enthalpy h_s and the total enthalpy of the mixture H usually have the dimensions J/kg-mole; mass-specific values are denoted by the symbol $\hat{}$, e.g., \hat{h} . The mass-averaged diffusion velocity of the s -th species is denoted by u_s^i . The body force \mathcal{F}_s , which might represent gravitational forces or an externally applied electromagnetic field, is often neglected. The viscosity of the gas mixture is represented by η , and the thermal conductivity of the l th energy mode by λ^l . The number of nonequilibrium energy modes is denoted by N_l .

The conservation equations stated above are quite general; they are limited by the assumptions that the medium is a continuum and that it is possible to define a translational temperature T which is locally isotropic. In addition, it is assumed that the molecules possess internal degrees of freedom and associated internal energies which may be characterized by Boltzmann temperatures T_l . These internal temperatures may differ from each other and from the translational temperature T . If thermal nonequilibrium is to be simulated, a separate conservation equation (Refs. 8-9)

$$\frac{\partial(\rho \hat{e}^l)}{\partial t} + \nabla_i(\rho \hat{e}^l U^i) = \nabla_i(\lambda^l \nabla^i T_l) - \nabla_i(\sum_{s=1}^{N_s} \rho_s \hat{e}_s^l u_s^i) + \dot{\omega}^l, \quad (6)$$

with a source term, $\dot{\omega}^l \equiv \sum_{s=m}^n \dot{\omega}_s^l$, must be added for each assumed nonequilibrium internal energy mode. The limits m and n will, in general, depend on l . Each source term may be a sum of several effects. For instance, if vibration can be described as a Boltzmann distribution with a parameter $T_v \neq T$, the vibrational energy equation for species s would be

$$\frac{\partial(\rho_s \hat{e}_s^v)}{\partial t} + \nabla_i(\rho_s \hat{e}_s^v U^i) = \nabla_i(\lambda^v \nabla^i T_{v,s}) - \nabla_i(\rho_s \hat{e}_s^v u_s^i) + \dot{\omega}_s^v \quad (7)$$

where the source term might be

$$\dot{\omega}_s^v = S_s^{v-T} + S_s^{v-v} + S_s^{v-e} + S_s^{v-c} \quad (8)$$

where S_s^{v-T} represents the interaction with the translational energy, which is modeled in NEQPAK with the Landau-Teller theory, S_s^{v-v} represents the resonant interchange of vibrational energy with other vibrators, and S_s^{v-e} is the energy gain by electron impact. The final term of Eq. (8), S_s^{v-c} , represents the effect of chemical changes affecting the population of species s . Since dissociation of vibrationally excited molecules is more likely and recombination probably leaves the product molecule in an excited state, the average amount of vibrational energy transferred by chemical interaction is not clear at the present time. NEQPAK, therefore, offers the user a choice among the formulae advocated in Refs. 10-12. If the vibrational energy has a non-Boltzmann distribution, the last term of Eq. (8), as programmed in NEQPAK, should be replaced, but the other three terms would still apply. It is frequently necessary to provide a conservation equation with source term,

$$\dot{\omega}_e^e = S_e^{e-T} - S_e^{e-c} - \sum_{molecules} S_i^{v-e} \quad (9)$$

for the translational energy of the free electron, which is affected by collision with heavy particles S_e^{e-T} , by impact ionization S_e^{e-c} , and by excitation of the vibrational levels of the heavy species, $\sum_{molecules} S_i^{v-e}$. Both vibrational and electronic excitation energy are affected by the emission and absorption of radiant energy, but these effects are not fully implemented in NEQPAK.

The foregoing source terms are described in more detail in Secs. 2.5 and 2.6. The implementation of these source terms within NEQPAK is described in Secs. 3.4 and 3.5.

The conservation equations must be supplemented by the thermal equation of state, Eq. (1), and a caloric state equation,

$$h_s = h_s(T, T_l) = e_s + \mathcal{R}T \quad (10)$$

for each species. Since the thermal energy is a nonlinear function of the temperature for all species except the electron, it is supplied by NEQPAK.

The species conservation equations are often written in terms of species densities $\rho_s = \gamma_s \mathcal{M}_s$, where \mathcal{M}_s is the molecular weight of species s . Another common composition variable, useful where the flow solver does not require conservation form, is $\hat{\gamma}_s = \gamma_s / \rho$ where $\rho = \sum_{s=1}^{N_s} \rho_s$ is the mixture density. Mass fractions $Y_s = \rho_s / \rho$ and mole fractions $X_s = \gamma_s / \sum_s \gamma_s$ are sometimes employed; they have the advantage of displaying chemical processes independently of the density changes caused by the flow. Note that the conserved variable, whatever the composition or energy units, is always a density: number density, mass density, or energy density.

The flow equations have been introduced here to define the notation and to supply a framework for the discussion of NEQPAK capabilities. NEQPAK does not undertake to solve these equations; it is a set of tools designed to save the code developer time and effort by eliminating the requirement for developing thermal and chemical routines.

2.1.1 Boundary Conditions

The conservation and state equations must, of course, be supplemented by boundary conditions for each variable. Even if one neglects injection, ablation, and surface combustion, the ability of a solid surface to absorb energy and to accumulate atoms and free radicals profoundly affects the chemical processes in its immediate vicinity. One common treatment of these wall catalytic effects is to assume that the gas at the wall is in complete thermochemical equilibrium at the local wall temperature and pressure. NEQPAK has the capability, described in Sec. 3.2.2, of generating a table of equilibrium compositions corresponding to specified pressures and temperatures.

2.2 THERMAL MODELS

The number and complexity of the internal energy conservation equations have stimulated the formulation of numerous approximate models. For instance, Lee's thermal model (Ref. 8) assumes that the vibrational energies of all diatomic air species may be categorized by the same Boltzmann temperature T_v , and that the Boltzmann temperature T_e , which describes the populations of the bound electronic states of all of the heavy particles, is assumed to be the same as the translational temperature of the free electrons. Park (Refs. 13-14) makes the further simplification that $T_e = T_v = T_v$. On the other hand, Candler and MacCormack (Ref. 15) have sought a greater realism by assigning separate vibrational temperatures to some of the species. All of these models assume that the rotational degrees of freedom are in equilibrium with the translational temperature and that the separate energy storage modes are independent. Liu and Vinokur (Ref. 16) argue that the known dependence of the vibrational

potential energy upon both the rotational and electronic state indicates that only a single internal energy mode should be considered. The following thermal models are embodied in NEQPAK:

- Model 1 corresponds to complete thermal equilibrium. All of the internal energy modes of all species are in equilibrium with the translational temperature T . Thus, only one energy equation, Eq. (5), is needed.
- Model 2 corresponds to Park's two-temperature model (Refs. 13-14) as discussed in Ref. 9. The translational and rotational modes are assumed to be in equilibrium with the translational temperature. The electronic excitation energy of all species and the vibrational energies of the polyatomic species are calculated with T_v as is the translational energy of the free electrons. Thus,

$$h_s = \underbrace{\int_0^T C_{p,s}^{tr} dT'}_{h_s^{tr}} + h_{0,s}^0 + \underbrace{\int_0^{T_v} C_{p,s}^v dT'}_{h_s^v} \quad (11)$$

where $h_{0,s}^0$ is the molar heat of formation at 0 K and 1 atm, $C_{p,s}^{tr}$ is the (constant) heat capacity of the translation-rotation mode, and $C_{p,s}^v$ is the molar heat capacity of the vibration and electronic excitation modes. Note that the heat of formation is assigned to the h_s^{tr} term. For species other than the electron, the "pV work" term $\mathcal{R}T$ is assigned to h_s^{tr} . In the case of the free electron, the term $\mathcal{R}T_e$ is grouped with h_e^v for Model 2 and with h_e^e for Models 3 and 4. In addition to Eq. (5), a conservation equation for the mixture internal energy $\hat{e}^V = \sum_{s=1}^{N_s} Y_s \hat{e}_s^V$ must be supplied. The source term $\dot{\omega}^V$ is formed by summing the vibrational source terms, Eq. (8), over the N_v molecules and adding the free electron source term, Eq. (9). In the summation, the S_i^{v-e} terms cancel out.

- Model 3 corresponds to the three-temperature model suggested by Lee (Ref. 8) in which the distribution of vibrational energy among the available states for each molecule is described by the single Boltzmann temperature T_v , and the populations of the excited electronic states of all species are described by the Boltzmann temperature T_e . The kinetic energy of the free electron is assumed to be in equilibrium with this electronic temperature. Thus,

$$h_s = h_s^{tr} + \underbrace{\int_0^{T_v} C_{p,s}^v dT'}_{h_s^{v-e}} + \underbrace{\int_0^{T_e} C_{p,s}^e dT'}_{h_s^e} \quad (12)$$

where $C_{p,s}^v$ and $C_{p,s}^e$ are the corresponding heat capacities. Three energy equations, one for the total energy, Eq. (5), one for the mixture vibrational energy $\Sigma_{molecules} \gamma_s \hat{e}_s^v$, and one for the electron-electronic energy, are needed.

- Model 4 corresponds to the model employed by Candler and MacCormack (Ref. 15) in which a separate vibrational temperature $T_{v,s}$ is assigned to each of N_v molecules. The vibrational energy of the remaining molecules is assumed to be in equilibrium with the translational temperature. All species share the same electron temperature T_e . There will be one total energy equation, one mixture electron-electronic energy equation, and n_v vibrational energy equations with source terms given in Eq. (8).

2.3 TRANSPORT PROPERTIES

The species diffusion velocity u_s which appears in Eqs. (3), (5), and (6) is determined from

$$\sum_{n=1}^{N_s} \frac{\chi_n \chi_s}{\mathcal{D}_{s,n}} (u_n - u_s) = d_s - \left[\sum_{n=1}^{N_s} \frac{\chi_s \chi_n}{\mathcal{D}_{s,n}} \left(\frac{D_n^T}{\rho_n} - \frac{D_s^T}{\rho_s} \right) \right] \nabla \ln T, \quad (13)$$

with

$$d_s = \nabla \chi_s + (\chi_s - Y_s) \nabla \ln p - Y_s (\rho \hat{\mathcal{F}}_s - \sum_k \rho_k \hat{\mathcal{F}}_k) / p \quad (14)$$

where $\hat{\mathcal{F}}_s$ is the body force per unit mass, χ_s is the mole fraction of species s in the mixture, and Y_s is the mass fraction. In addition, the binary diffusion coefficients are denoted by $\mathcal{D}_{l,m}$ and the thermal diffusion coefficients by D_m^T .

Since the solution of Eq. (13) is time consuming, it is customary to introduce the approximation (Ref. 17)

$$\chi_s u_s = -D_s d_s \quad (15)$$

where

$$D_s = \frac{1 - Y_s}{\sum_{n \neq s} \frac{\chi_n}{\mathcal{D}_{n,s}}} \quad (16)$$

and d_s is defined in Eq. (14). The quantity D_s is called the effective diffusion coefficient for species s . Although Eq. (15) was derived under the assumption that only a trace amount of species s is present in the mixture, the diffusion velocities calculated with Eq. (15) agree well with an exact solution of Eq. (13) for air at $T = 8141.6$ K as shown in Table 1. The indicated errors in Table 1 are no worse than the uncertainties in the binary diffusion coefficients. This agreement may be expected when the molecular masses of all species are of the same order of magnitude (Ref. 18). If the molecular masses differ widely, use of the effective diffusion coefficients sometimes produces serious local errors in the composition and in mass conservation (Ref. 19). Moss (Ref. 20) found that the inclusion of the full multicomponent diffusion mechanism made essentially no difference in his high-altitude viscous shock layer solutions.

Table 1. Comparison of Diffusion Velocities for High-Temperature Air

	E -	N	O	O ₂	N ₂	NO	NO +
Mole%	4.488E-04	3.225E-01	2.785E-01	4.225E-04	3.384E-01	1.405E-02	4.488E-04
Eqs. (13)-(14)	-6.772E-01	-2.690E-03	-1.490E-03	7.485E-04	1.720E-03	7.652E-04	-2.176E-03
Eqs. (15)-(16)	-6.770E-01	-2.580E-03	-1.322E-03	8.676E-04	1.736E-03	9.415E-04	-1.458E-03

The term in d_s , Eq. (14), which is proportional to $\nabla \ln p$, is customarily neglected. The thermal diffusion term in Eq. (13) is usually insignificant compared to the species gradient term and will be neglected here.

In an ionized gas, the strong electrostatic forces between positive and negative ions tend to give these particles a common velocity. This effect is known as ambipolar diffusion and applies everywhere except very close to a solid wall. The limiting distance is the Debye length, L

$$L = 69 \sqrt{T_e / n_e} \quad (17)$$

where T_e is the electron temperature in K and n_e is the electron number density in m^{-3} . It is shown in Appendix A that this ambipolar diffusion introduces a further coupling between the species equations, Eq. (3), which must now be rewritten

$$\frac{\partial \gamma_s}{\partial t} + \nabla \cdot (\gamma_s \vec{U}_s) = \dot{w}_s + \nabla \cdot \left[\Gamma (D_s \nabla \chi_s - \frac{\alpha_{e,s} \mu_s \gamma_s}{\sum_{s=1}^{N_s} \mu_s \gamma_s \alpha_{e,s}^2} \sum_r \alpha_{e,r} D_r \nabla \chi_r) \right] \quad (18)$$

where $\alpha_{e,s}$ is the number of excess electrons in species s and is negative for a positive ion, $\Gamma = \sum_{j=1}^{N_s} \gamma_j$, and μ_s is the ionic mobility of species s and is related to the effective diffusion coefficient by the "Einstein relation" (Ref. 21)

$$\mu_s = 11605.0 D_s / T. \quad (19)$$

Note that if only electrons and one species of positive ions are considered, Eq. (18) reduces to

$$\frac{\partial \gamma_+}{\partial t} + \nabla \cdot (\gamma_+ \vec{U}) = \dot{w}_+ + \nabla \cdot (\Gamma D_a \nabla \chi_+) \quad (20)$$

where

$$D_a \equiv \frac{D_+ \mu_e + \mu_+ D_e}{\mu_+ + \mu_e} \quad (21)$$

If it is assumed that $\mu_e \gg \mu_+$, $T_e \approx T$, and Einstein's relation, Eq. (19), is employed, the approximate result

$$D_a \approx 2D_+$$

used by Gnoffo, et al. (Ref. 9), is recovered.

Diffusion and viscosity depend only on the mass and motion of the molecules as a whole and are independent of the internal state. Thermal conductivity, on the other hand, is determined by the transport of energy — kinetic and internal — by the molecules.

Appendix B shows that the thermal conductivity of a pure species is related to the viscosity and molar heat capacity of the species by

$$\lambda_s = [3.75\eta_s + \rho\mathcal{D}_{s,s}(\frac{C_{p,s}}{\mathcal{R}} - 2.5)]\frac{\mathcal{R}}{\mathcal{M}_s} \quad (22)$$

The first term on the right side of Eq. (22) is the translational part λ_s^t of the “frozen” thermal conductivity and is unaffected by any thermal nonequilibrium. The second term, on the other hand, represents the contribution of the internal energy modes to the thermal conductivity and is, therefore, affected by thermal nonequilibrium through $C_{p,s}$. As written, Eq. (22) is applicable to a single-temperature thermal model. Note that in this case, $C_{p,s}$ represents the electronic excitation energy for both monatomic and polyatomic species as well as the vibrational and rotational energy modes. For multitemperature thermal models, a separate coefficient

$$\lambda_s^m = \rho\mathcal{D}_{s,s}\frac{C_{p,s}^m}{\mathcal{M}_s} \quad (23)$$

is calculated for each nonequilibrium mode.

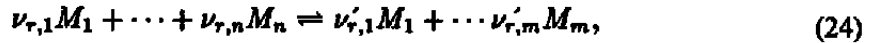
Note that the transport properties of the heavy species are evaluated with the translational temperature and that η_e and λ_e are evaluated with the translational temperature of the free electron T_e . For Model 1, the user must set $T_e = T$.

Only the viscosity and thermal conductivities of the mixture as a whole enter the conservation equations. The “exact” formulae for the viscosity and conductivity of a mixture in terms of the species properties (Ref. 7) are so unwieldy and computationally expensive that numerous approximations have been proposed. The procedures adopted in NEQPAK are those of Armaly and Sutton (Refs. 22–23) which are the only approximate rules to explicitly account for ionization. The algorithms suggested by Armaly and Sutton are too lengthy for discussion here.

Evaluation of transport properties using NEQPAK is discussed in Sec. 3.7.

2.4 CHEMICAL SOURCE TERMS

A typical reaction — the r th reaction — may be written in the form



in which M_i represents one mole of species i and the $\nu_{r,i}$ and $\nu'_{r,i}$ are the stoichiometric coefficients. The species on the left-hand side of Eq. (24) are called the reactants and those on the right-hand side are the products, although this nomenclature is arbitrary since the reaction is also going from right to left as indicated by the shorthand symbol \rightleftharpoons . The rate of disappearance of any species involved in the r th reaction is

$$\mathcal{L}_{r,s} = \nu'_{r,s}k_r^f \prod_{j=1}^{N_s} \gamma_j^{\nu'_{r,j}} + \nu_{r,s}k_r^f \prod_{j=1}^{N_s} \gamma_j^{\nu_{r,j}} \quad (25)$$

A product in reaction r appears at the rate

$$\mathcal{G}_{r,s} = \nu'_{r,s}k_r^f \prod_{i=1}^{N_s} \gamma_i^{\nu_{r,i}} + \nu_{r,s}k_r^f \prod_{i=1}^{N_s} \gamma_i^{\nu'_{r,i}}. \quad (26)$$

The net rate of change of species s due to all reactions is

$$\dot{w}_s = \sum_{r=1}^{N_r} (\mathcal{G}_{r,s} - \mathcal{L}_{r,s}). \quad (27)$$

where N_r is the number of reactions. Like most models of the aerothermochemical effects of atmospheric entry and combustion, NEQPAK assumes the modified Arrhenius form (Ref. 24) for chemical reaction rates

$$k_r^f = A_r T_q^{B_r} \exp(-C_r/T_q), \quad (28)$$

where T_q represents a generic temperature. The effects of thermal nonequilibrium on these rates are often modeled (Refs. 13–14) by using some blend of the translational and internal temperatures for T_q in certain reactions. Park's model (Ref. 13), for example, uses $T_q = T_e^\beta T^{1-\beta}$; $0 < \beta < 1$. The electron translational temperature T_e may be used as T_q for electron-impact ionization or dissociative recombination reactions. An alternative approach, explored in detail in Sec. 2.4.2, is to assume that Eq. (28) represents the rate for thermal equilibrium and must be corrected by a multiplicative "Vibrational Coupling Factor." This approach, proposed by Treanor and Marrone (Refs. 25–26), has been extended recently by Olynick and Hassan (Ref. 11) and by Knab, Frühauf, and Jonas (Ref. 10). The 'virtual species'

approach of Landrum and Candler (Ref. 12) results in rate equations which can be manipulated into the coupling factor form.

2.4.1 Calculation of Reverse Rates

The reverse reaction rate coefficient k_r^r is related to the forward rate by

$$k_r^r = k_r^f / K_r^c, \quad (29)$$

where

$$K_r^c = (p_{atm}/\mathcal{R}T)^{\delta_r} \exp(-\frac{\Delta F}{\mathcal{R}T}), \quad (30)$$

is the equilibrium constant for the r th reaction, and

$$\delta_r \equiv \sum_{i=1}^{N_s} (\nu_{r,i}' - \nu_{r,i}); \quad (31)$$

$$\Delta F \equiv \sum_{s=1}^{N_s} (\nu_{r,s}' - \nu_{r,s}) G_s^0$$

In Eq. (30), $p_{atm} = 1.01325 \times 10^5$ Pa. Also, G_s^0 is the standard-state Gibbs free energy for species s .

Many collections of reaction rate data provide explicit expressions of the Arrhenius form for the reverse rate coefficient. Explicit specification of both forward and reverse rates determines an equilibrium constant, through Eq. (29), and a Gibbs free energy, Eq. (30), which in general will differ from that calculated with the NEQPAK curve fits and may affect the calculated state of the gas.

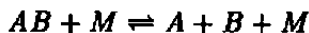
2.4.2 Vibrational Coupling

The vibrational coupling method of modeling the effect of vibrational excitation on chemical reaction rates assumes that the quoted rate coefficients were measured for a thermal equilibrium situation and multiplies Eq. (28) by a function of translational and vibrational temperatures. NEQPAK extends this model slightly to allow separate coupling factors for the forward and reverse directions.

Coupling models proposed by Olynick and Hassan (Ref. 11), by Landrum and Candler (Ref. 12), and by Knab, Frühauf, and Jonas (Ref. 10) are implemented in NEQPAK. The foregoing coupling models are mathematically consistent with the use of a common vibrational

temperature (Model 2 or Model 3), but the use of such a crude thermodynamic approximation largely negates any advantage which might be obtained from the use of these sophisticated coupling models. The Landrum-Candler and Knab-Frühauf-Jonas coupling models are implemented in NEQPAK only for complete vibrational nonequilibrium (Model 4).

Olynick—Hassan Coupling The Olynick-Hassan coupling model applies only to dissociation reactions



where molecule AB is a rotationless harmonic oscillator and M is an arbitrary third body. Since the analysis does not allow for population inversions, the Olynick-Hassan model is not valid for expanding flows.

Let $z = e_s^v / (\mathcal{R}T_v)$ and define

$$x = (1 - T_v/T)T_{d,s}/T_v$$

where $T_{d,s}$ is the dissociation temperature of AB. Then, the forward coupling factor is

$$\Psi_f = \frac{z\Gamma(z, x)}{x^z} \quad (32)$$

where $\Gamma(z, x)$ is the incomplete gamma function (Ref. 27). The reverse coupling factor is

$$\Psi_r = 1.0$$

Landrum-Candler The Landrum-Candler model was developed from an intensive theoretical investigation of the dissociation of N_2 . Its applicability to other diatomic species has not been investigated, so the generalization coded here may not be warranted. The essence of the model is to replace the ordinary dissociation by a two-step process



In Eq. (33), AB^* represents the AB molecules with vibrational quantum numbers $v \geq v_c = (T_{d,AB} - T)/\theta_{AB}$, where $T_{d,AB} = \Delta_{AB}/\mathcal{R}$ is the dissociation temperature. The molecules AB have a vibrational temperature $T_v \neq T$, but the virtual species AB^* is in thermal equilibrium. It follows that a vibrational coupling factor is needed only for AB. The coupling factor for the first of the reactions listed in Eq. (33) is

$$\Psi_f = \exp(\bar{\beta}\theta_s \frac{T - T_v}{T_v T}) \frac{\exp[-(v_c - 1)\theta_s/T_v]}{\mathcal{Z}_{AB}(v_c\theta_s, T_v)} \quad (34)$$

In Eq. (34), \mathcal{Z}_{AB} is the partition function for a harmonic oscillator truncated at a quantum number $l_{max} = [\epsilon/(\mathcal{R}\theta_{AB})] - 1$ below some cut-off energy ϵ , namely

$$\mathcal{Z}_{AB}(x, y) \equiv \sum_{l=0}^{l_{max}} e^{-l\theta_{AB}/y} = \frac{1 - e^{-x/y}}{1 - e^{-\theta_{AB}/y}} \quad (35)$$

where $x = l_{max}\theta_{AB}$, θ_{AB} is the characteristic temperature for oscillator AB , and y is a temperature-like function. The parameter $\bar{\beta}$ is supposed to correct for the anharmonicity of AB . Landrum and Candler were able to obtain impressive agreement with the full simulation results for N₂ by taking $\bar{\beta} = 5.0$ and increasing the Millikan-White (Ref. 28) vibrational relaxation time τ by a factor of 25.

Knab, Frühauf, and Jonas Knab, Frühauf, and Jonas (Ref. 10) have extended the concept of vibrational coupling to reaction types other than dissociation. Table 2 shows for each type the coupling factors $\Psi_i(T, T_v)$ recommended by Knab, et al.

Table 2. Coupling Factors for Various Reaction Types

Reaction	Forward Rate	Reverse Rate
$AB + M \rightleftharpoons A + B + M$	$\Psi_4 k_r^f$	k_r^r
$AB + C \rightleftharpoons AC + B$	$\Psi_3 k_r^f(T)$	$\Psi_5 k_r^r(T)$
$A + B \rightleftharpoons AB^+ + E^-$	$k_r^f(T)$	$\Psi_5 k_r^r(T_e)$

In Table 2, k_r^f and k_r^r are the ordinary equilibrium reaction rates in the Arrhenius form. The Ψ functions are defined as follows:

$$\Psi_3 = \frac{\mathcal{Z}_{AB}(T_{d,AB}, T)}{\mathcal{Z}_{AB}(T_{d,AB}, T_v)} \times \frac{e^{-a_r/T} \mathcal{Z}_{AB}(a_r, g) + \mathcal{Z}_{AB}(T_{d,AB}, T_{0,r}) - \mathcal{Z}_{AB}(a_r, T_{0,r})}{e^{-a_r/T} \mathcal{Z}_{AB}(a_r, -\phi_r) + \mathcal{Z}_{AB}(T_{d,AB}, T^*) - \mathcal{Z}_{AB}(a_r, T^*)} \quad (36)$$

$$\Psi_4 = \frac{\mathcal{Z}_{AB}(T_{d,AB}, T)}{\mathcal{Z}_{AB}(T_{d,AB}, T_{v,AB})} \times \frac{e^{-\alpha T_{d,AB}/T} \mathcal{Z}_{AB}(\alpha T_{d,AB}, g_{AB}) + \mathcal{Z}_{AB}(T_{d,AB}, T_{0,r}) - \mathcal{Z}_{AB}(\alpha T_{d,AB}, T_{0,r})}{e^{-\alpha T_{d,AB}/T} \mathcal{Z}_{AB}(\alpha T_{d,AB}, -\phi_r) + \mathcal{Z}_{AB}(T_{d,AB}, T^*) - \mathcal{Z}_{AB}(\alpha T_{d,AB}, T^*)} \quad (37)$$

$$\Psi_5 = \frac{\mathcal{Z}_s(T_{d,s}, T) \mathcal{Z}_s(T_{d,s}, T_{0,r})}{\mathcal{Z}_s(T_{d,s}, T_{v,s}) \mathcal{Z}_s(T_{d,s}, T^*)} \quad (38)$$

where s represents the molecule or ion on the right side of the reaction. The pseudo-temperatures g_r , $T_{0,r}$, and T^* used in Eqs. (36)–(38) are

$$\frac{1}{g_r} = \frac{1}{T_{v,s}} - \frac{1}{T} - \frac{1}{\phi_r} \quad (39)$$

$$\frac{1}{T_{0,r}} = \frac{1}{T_{v,s}} - \frac{1}{\phi_r} \quad (40)$$

$$\frac{1}{T^*} = \frac{1}{T} - \frac{1}{\phi_r} \quad (41)$$

The input parameter ϕ_r measures the probability that a molecule in vibrational state l will dissociate. If $\phi_r = \infty$, dissociation is equally probable from all vibrational levels. Knab, et al. also introduce an effective activation temperature $a_r = \alpha C_r$ for reaction r . If $\alpha = 1$, the formulation of Eq. (37) reduces to that of Treanor and Marrone (Ref. 25).

For associative ionization reactions, the vibrational coupling factor for the reverse direction is just the Ψ_5 function defined in Eq. (38) above with the translational temperature T replaced with the electron temperature T_e .

2.5 VIBRATIONAL ENERGY SOURCE TERMS

The species vibrational energy is affected by inelastic collisions with heavy molecules and with electrons. During a heavy particle collision there may be an exchange of vibrational energy. The species vibrational energy is also affected by an increase or decrease in the number of vibrationally excited molecules through chemical reaction. Interaction with the electromagnetic field is not modeled at the present time.

2.5.1 V-T Interaction

Landau and Teller (Ref. 29) showed that if the vibrational energy levels are equally spaced (harmonic oscillator) and only single-level transitions are allowed, then

$$S_s^{v-T} = \gamma_s \frac{(e_s^{v*} - e_s^v)}{\tau_s} \quad (42)$$

where the e_s^{v*} indicates the equilibrium value of the vibrational energy, and τ_s is the so-called relaxation time. Strictly speaking, Eq. (42) is valid only for a harmonic oscillator, but it is applied to anharmonic oscillators by using the polynomial curve fits defined in Sec. 2.7 to calculate the equilibrium vibrational energy e_s^{v*} .

The relaxation time $\tau_{s,j}$ of species s in a bath of species j is calculated using the expression

$$p\tau_{s,j} = \tau_{s,j}^a T^{\tau_{s,j}^b} \exp(\tau_{s,j}^c / T^{\tau_{s,j}^d}) \quad (43)$$

where p is the pressure. The relaxation time employed in Eq. (42) is

$$\tau_s = \sum_{i=1}^{N_s} \chi_i \tau_{s,i} + \tau_s^P \quad (44)$$

where

$$\tau_s^P = C \sqrt{\frac{\mathcal{M}_s}{T}} \frac{1}{\gamma_s} \quad (45)$$

is Park's high-temperature correction (Ref.14), and

$$C = (\sigma_s \mathcal{N} \sqrt{8\mathcal{R}/\pi})^{-1} = 2.898677 \times 10^{-7}$$

in SI units. The value $\sigma_s = 10^{-20} \text{ m}^2$ for the effective cross section is that suggested by Gnoffo, et al. (Ref. 9).

The necessary coefficients for a particular interaction pair may be generated by making use of the Millikan and White correlations (Ref. 28):

$$p\tau_{i,j} = \exp[A_{i,j}T^{-1/3} - 0.015A_{i,j}\mu^{1/4} - 18.42] \quad (46)$$

and

$$A_{i,j} = 0.00116\mu_{i,j}^{1/2}\theta_i^{4/3} \quad (47)$$

where p is the pressure in atmospheres and μ is the reduced mass of the mixture. In Eq. (47), $\theta_i = h\nu_i/\kappa$, where ν_i is the characteristic vibrational frequency, h is Planck's constant, and κ is the Boltzmann constant. Also, $\mu_{i,j}$ is the reduced mass of the interacting molecules i and j .

2.5.2 V-E Interaction

An encounter between a free electron and a molecule may result in the transfer of kinetic energy from the electron to a vibrational mode of the heavy particle. The probability for such an interaction is an extremely irregular function of the electron kinetic energy. Nevertheless, Lee (Refs. 8 and 30) has been able to model the process with an equation of the Landau-Teller type, [see Eq. (42)], namely

$$S_s^{v \leftarrow e} = \gamma_s \frac{e_s^{v**} - e_s^v}{\tau_{e,s}} \quad (48)$$

where e_s^{v**} is the vibrational energy evaluated at the electron temperature and the relaxation time is

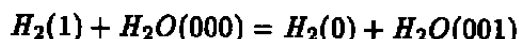
$$\tau_{e,s} = \frac{2}{n_e (1 - e^{-\theta_s/T_e})^2 \int k_{0,v} v^2 dv} \quad (49)$$

where n_e is the electron number density, θ_s is the characteristic vibrational temperature of species s , and $k_{0,v}$ is the rate constant for a transition from the vibrational ground state to vibrational level v .

Since the vibrational energy gained by the molecule is lost by the electron, V-E interactions need not be calculated for Model 2, in which vibrational and electron energy are pooled.

2.5.3 V-V Interaction

It is possible for two molecules to exchange vibrational energy during a collision, but this process is unlikely unless the molecules happen to have vibrational levels v_1 and v_2 with nearly the same energy. This vibrational exchange may be described as a reaction such as



which describes the interchange of vibrational energy between H_2 and one of the modes of H_2O . Rate data for such V-V reactions are available (Ref. 31), but considering level-to-level transitions of the kind indicated is computationally expensive. Therefore, NEQPAK has adopted the model of Candler and MacCormack (Ref. 15) in the form proposed by Knab, et al. (Ref. 10)

$$S_i^{v \leftarrow v} = \gamma_i \sum_{j \neq i} \mathcal{N}_{\sigma_{i,j}} \sqrt{\frac{8\mathcal{R}T}{\pi\mu_{i,j}}} \gamma_j (\mathcal{P}_{i,j} e_j - \mathcal{P}_{j,i} e_i) \quad (50)$$

where

$$\mathcal{P}_{i,j} = \mathcal{P}_{j,i} \frac{\theta_i e^{\theta_i/T} - 1}{\theta_j e^{\theta_j/T} - 1}$$

and $\mathcal{P}_{j,i} = 0.01$ are the exchange probabilities averaged over all vibrational energy levels.

2.5.4 V-C Interactions

It is clear that the dissociation of a vibrating molecule removes its vibrational energy from the species pool and that the formation of a new molecule must add some vibrational energy to the pool. The simplest assumption is that the energy gained or lost during the reaction is just the average vibrational energy e_s^v of the species, namely

$$S_s^{v-c} = \dot{w}_s e_s^v \quad (51)$$

This “nonpreferential dissociation” assumption is appropriate for Models 2 and 3 and also for the Olynick-Hassan coupling (Ref. 11) discussed in Sec. 2.4.2.

Landrum—Candler Coupling The Landrum-Candler theory (Sec. 2.4.2) assumes that the lower vibrational energy levels $v < v_c$ relax according to the Landau-Teller theory while the upper vibrational levels (the virtual species AB^*) are in thermal equilibrium. The critical level is

$$v_c = \frac{\epsilon_{AB} - T}{\theta_{AB}} + 1$$

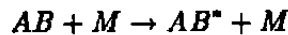
where ϵ_{AB} is the dissociation temperature and θ_{AB} is the characteristic vibrational temperature for species s . The level spacing of the virtual species is $\theta_{AB^*} = h_r \theta_{AB}$ where $h_r \approx 0.4$ is an input parameter. Thus, the rate of change of vibrational energy is

$$\gamma_{AB} \frac{de_s^v}{dt} = \gamma_{AB} \frac{(e_{AB^*}^{v*} - e_{AB}^v)}{\tau_{AB}} + S_{AB}^{v-c} \quad (52)$$

where

$$S_{AB}^{v-c} = \frac{\mathcal{R} v_c \theta_{AB}}{\tau} \left(\frac{\gamma_{AB}}{x} - \frac{F \gamma_{AB^*}}{y} \right) + \mathcal{R} v_c \theta_{AB} (\mathcal{G}_{r,s} - \mathcal{L}_{r,s}) \quad (53)$$

In Eq. (53), $x = \exp(v_c \theta_{AB}/T) - 1$ and $y = 1 - \exp(-\theta_{AB}/T)$. The reaction r is



The function F is defined as

$$F = \frac{\exp(-\theta_{AB^*}/T)}{Z(a, T)}$$

where

$$Z(a, T) = \exp(-(v_c - 1)\theta_{AB^*}/T) \frac{1 - e^{-a/T}}{e^{\theta_{AB^*}/T} - 1}$$

and $a = (v_m + 1 - v_c)\theta_{AB^*}$.

KFJ Coupling Unlike the other coupling theories described above, in the KFJ theory (Ref. 10) the vibrational coupling factor depends on both the translational and the species vibrational temperatures. Thus, in terms of the gain and loss rates introduced in Sec. 2.4,

$$S_{r,s}^{v-c} = f(T, T_{v,s})(G_{r,s} - L_{r,s}) \quad (54)$$

where $f(T, T_{v,s})$ is the quantity $G_{va,s}^{\alpha A}$ defined by Eqs. (48) and (49) of Ref. 10. The input parameter α is defined in Sec. 2.4.2 as are the pseudo-temperatures $\Gamma \equiv g_r$, $U \equiv \phi_r$, and $T_{0,r}$. The source term of Eq. (54) applies only to the reactions listed in Table 2. The total source term for e_s^v is formed by summing $s_{r,s}^{v-c}$ over all reactions.

2.6 ELECTRON-ELECTRONIC ENERGY SOURCE TERMS

The energy of the free electron is affected by elastic and inelastic collisions with heavy particles, by electron production, by interaction with applied and induced electric fields, and by radiation processes. The energy of electronic excitation may be lost to radiation. Of these effects, only those dealing with collisions and electron production are included among the NEQPAK source terms [$\dot{\omega}'$ of Eq. (6)].

Elastic collisions between electrons and heavy particles cause an energy exchange described by term 6 in Eq. (4) of Ref. 9, namely

$$S_e^{e-T} = 3\mathcal{R}\mathcal{M}_e\gamma_e(T - T_e) \sum_{s=2}^{N_s} \frac{f_{es}}{\mathcal{M}_s} \quad (55)$$

where f_{es} is the collision frequency defined by

$$f_{es} = \xi_1 \frac{\gamma_s}{T_e^{3/2}} \ln(\xi_2 \frac{T_e^3}{\gamma_e}) \quad (56)$$

for collisions with charged particles and

$$f_{es} = \xi_3 \sigma \gamma_s \sqrt{T_e} \quad (57)$$

for collisions with neutral particles. The constants ξ_1 , ξ_2 , and ξ_3 are defined as

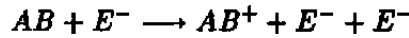
$$\xi_1 = 8 \sqrt{\pi / m_e} \frac{\mathcal{N} e^4}{3(2\kappa)^{1.5}} \quad (58)$$

$$\xi_2 = \kappa^3 / (\pi \mathcal{N} e^6) \quad (59)$$

$$\xi_3 = \mathcal{N} \sqrt{8\kappa / (\pi m_e)} \quad (60)$$

where m_e is the mass of the electron, κ is Boltzmann's constant, and e is the elementary charge. The effective cross section σ is computed with quadratic fits taken from Ref. 9.

Electron impact ionization, i.e., a process such as



leads to an electron energy loss

$$S_e^{e-c} = \gamma_1 \sum_{r=1}^{N_r} \sum_{s=2}^{N_s} \nu_{r,s} \nu_{r,1} \frac{\nu_{r,e}}{2} k_r^f \gamma_s \mathcal{I}_s \quad (61)$$

In Eq. (61), k_r^f is the forward rate coefficient defined in Eq. (28) and \mathcal{I}_s is the ionization energy per kg-mole of species s . The product of stoichiometric factors will vanish except for impact ionization reactions.

2.7 THE MATERIAL PROPERTIES DATABASE

Post-shock temperatures in the flow field of a reentering planetary vehicle can approach 50,000 K. While direct calorimetric measurements at such temperatures are clearly impossible, it is possible to use spectroscopic data and the methods of statistical mechanics to infer thermal properties at reentry conditions. The most extensive tables of thermodynamic properties at very high temperatures are those of Browne (Refs. 32–35), who used low-temperature measurements to evaluate the parameters of the Morse potential from which he calculated the second virial coefficient and the partition function (Ref. 36). This approach has been criticized by Jaffe (Ref. 37) on the grounds that it does not account for the effect of excited electronic states on rotational-vibrational potential energy and that it neglects the effect of

finite dissociation energy on the partition function. The most accurate calculations (limited apparently to N_2) are those of Ref. 38, which involved thousands of numerical solutions of the Schrödinger wave equation.

A computational effort of the scale outlined above is clearly impracticable for all of the polyatomic and ionized species in the NEQPAK database. Moreover, the necessary spectral data are not available for many of the species of interest. The JANAF tables (Ref. 39) contain tabulated thermodynamic data over the range $0 \leq T \leq 6,000$ K for over 600 species. Polynomial fits to the JANAF data are presented by Svehla, et al. (Ref. 40). Esch, et al. (Ref. 41) have extended these fits to 15,000 K for selected species of special interest to the aerospace community. Gupta, et al. (Ref. 42) have obtained polynomial fits to Browne's data up to 35,000 K for 11 air species. Because of the limited range and inconsistent quality of the published data, many of the thermodynamic property tables in NEQPAK have been recomputed using the methods of Ref. 43 with molecular constants taken from Refs. 39 and 44. The calculations were extended to 30,000 K in order to ensure that the polynomial approximations yielded reasonable values at typical post-shock temperatures.

In order to minimize memory requirements, the thermal data are stored in the form of multisegment polynomials

$$\frac{C_{p,s}}{\mathcal{R}} = a_{1,s} + a_{2,s}T + a_{3,s}T^2 + a_{4,s}T^3 + a_{5,s}T^4 \quad (62)$$

$$\frac{h_s}{\mathcal{R}T} = a_{1,s} + \frac{a_{2,s}}{2}T + \frac{a_{3,s}}{3}T^2 + \frac{a_{4,s}}{4}T^3 + \frac{a_{5,s}}{5}T^4 + \frac{a_{6,s}}{T} \quad (63)$$

$$\frac{G_s^0}{\mathcal{R}T} = a_{1,s}(1 - \ln T) - \left(\frac{a_{2,s}}{2}T + \frac{a_{3,s}}{6}T^2 + \frac{a_{4,s}}{12}T^3 + \frac{a_{5,s}}{20}T^4 + \frac{a_{6,s}}{T} \right) - a_{7,s} \quad (64)$$

There are up to six segments for each species. The junction temperatures, which differ from species to species, mark the upper limit of applicability of a given set of coefficients.

Since the convergence of iterative processes involving the thermal properties may be hindered by discontinuities in the data, great care was taken to maintain continuity at the junction points. A special least-squares routine which enforced continuity of value and slope at the junctions was used to calculate the coefficients a_1, \dots, a_7 . Smoothness at the junction points was further improved by making slight adjustments in a_6 and a_7 . The heat of formation at absolute zero clearly dictates the value of a_6 for the first segment.

Figure 2 is a plot of the dimensionless specific heat of NO as calculated by Jaffe (Ref. 37), by Browne (Ref. 32), and with the polynomial fits used in NEQPAK. The quality of the NEQPAK fits to the enthalpy may be assessed from Table 3.

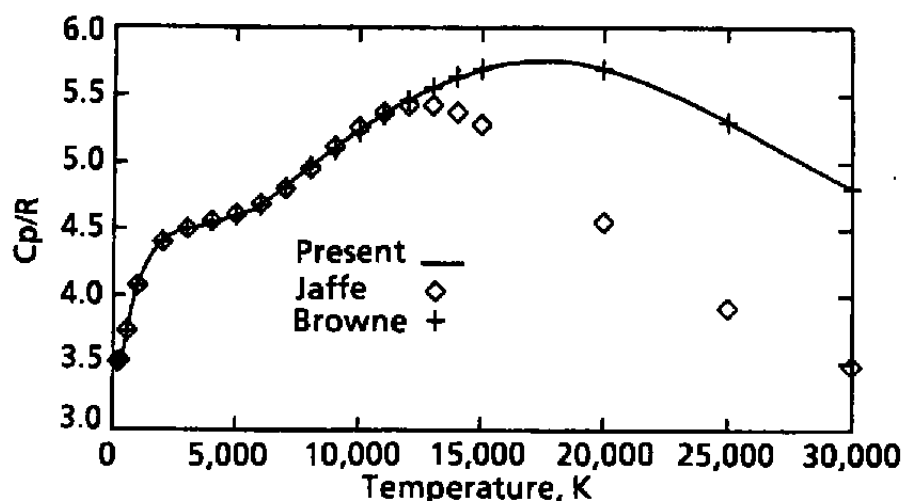


Figure 1. Heat capacity of NO.

Table 3. Fit Quality for NO

Junction Temperature	$\frac{h_{upper} - h_{lower}}{h_{lower}}$
300.00	1.1508×10^{-5}
1000.0	-2.8633×10^{-6}
5000.0	2.0833×10^{-7}
15000.0	4.1667×10^{-8}
25000.0	5.8333×10^{-8}

Average error 0.195%

Maximum error 0.581%

The database also contains the coefficients for polynomial fits to the natural logarithms of the binary diffusion coefficients and viscosities. These fits are from various sources. The fit coefficients for the eleven air species O_2 , N_2 , O , NO , NO^+ , O_2^+ , N_2^+ , O^+ , N^+ , and E^- are taken directly from Ref. 42. Although Ref. 42 recommends the use of the Sutherland formula for air viscosities at $T < 1,000$ K, numerical experiments at AEDC show that the

tabulated fits work well at room temperature or above. The viscosity of neutral particles other than the air species and the binary diffusion coefficients involving these species were calculated with the program of Ref. 19. Interactions between charged and neutral particles were evaluated with the program of Ref. 45. Charged-charged interactions were calculated with a special code based on the formulae of Devoto (Ref. 46).

The transport properties of the individual species are calculated with the following curve-fit expressions (Ref. 42):

$$\eta_s = 0.1 \exp(b_{5,s} + b_{4,s}T + b_{3,s}T^2 + b_{2,s}T^3 + b_{1,s}T^4) \quad (65)$$

$$\mathcal{D}_{i,j} = \frac{10.1325}{p} S \exp(d_{4,i,j} + d_{3,i,j}T + d_{2,i,j}T^2 + d_{1,i,j}T^3), \quad (66)$$

where $T = \ln T$ and S is the electrostatic shielding ratio, namely

$$S = \begin{cases} 1 & \text{for neutral-particle interactions} \\ \frac{1}{\ln \Lambda(T/p_e^{1/4})} & \text{if either particle is charged} \end{cases}$$

The shielding function $\Lambda(x)$ is defined as

$$\Lambda(x) = (2.09 \times 10^{-14}x^4 + 1.52 \times 10^{-8}x^{8/3})^{1/2}$$

and $p_e = \gamma_e \mathcal{R}T_e / 1.01325 \times 10^5$ is the electron partial pressure expressed in atmospheres.

3.0 USING NEQPAK

3.1 STRUCTURE

The data flow within NEQPAK is shown in Fig. 2. The modules NPCHEMIN and NPREPEQ shown in the bottom tier of Fig. 2 are "setup" routines called by the flow solver or a preprocessor to interpret the chemical model and to prepare the necessary constants and tables. These setup routines need be called only once while modules in the upper tier are tools which are called repeatedly by the flow solver. Since it is impossible to name all of the "tool" routines in the limited space of the diagram, only the broad categories are shown. The use of these tools is explained fully in the following sections.

NPCHEMIN (Sec. 3.2.1) reads the user-supplied reaction mechanism from the file assigned to unit number INPR, extracts the necessary information from the material properties database on unit numbers INPTH and INREL and puts the necessary constants and tables into the common blocks /NAMES/ and /NEQCOM/. The thermal model and the names and

concentrations of any inert species are calling arguments of NPCHEMIN. In addition, if Model 4 is selected, the names of the N_v nonequilibrium vibrators must be specified by the user.

The two common blocks /NAMES/ and /NEQCOM/ contain only the thermochemical and transport properties for the current problem. The variables in common block /NEQCOM/ are defined in Appendix C.

Subroutine NPPEPEQ (Sec. 3.2.2) uses the thermochemical properties in the common blocks to generate a table of equilibrium compositions which is stored on unit IEQ. Interpolation within this table is performed by Subroutine NPEQCOMP (Sec. 3.9). A third common block /EQCOM/ contains information relative to the number and spacing of the pressures and temperatures for which equilibrium composition data are tabulated.

All data stored by the flow solver at points of the computational grid, such as local values for temperature, energy, and composition, are communicated through the subroutine argument lists. In order to save memory, these data are passed to the various NEQPAK subroutines in arrays of vector length NP rather than passing the data for the entire grid. In a flow solver, NP would ordinarily be one of the grid dimensions. The index referring to the grid dimension is always the last subscript of the array. Array dimensions are either passed through the subroutine arguments or are set by the parameter statement in file NPDIMEN which is included in every routine. Table 4 lists the current default values for the array dimensions. Since some flow solvers use a leap-frog procedure, the arguments of all subroutines dealing with grid-dependent arrays contain the sequence "LOW,NP,INC" in which LOW is the index of the initial point, NP is the index of the final point, and INC is the increment for "DO-loops."

Computation has been vectorized as far as possible. This vectorization will be most efficient when the number of grid points — always the innermost loop — exceeds the number of species or reactions.

SI units are used exclusively in NEQPAK. The composition variable is the concentration in $kg\text{-moles}/m^3$. Energies are expressed in $J/kg\text{-mole}$ or in J/m^3 . Reaction rates may be entered in $cm^3/gm\text{-mole}/s$ or in $cm^3/particle/s$, but these will be converted to SI units before being used for calculation.

Apart from error messages, only the "set-up" modules, NPCHEMIN and NPPEPEQ, write to standard output. NPPEPEQ also writes to unit IEQ. Detailed descriptions of the various NEQPAK routines are given in the following subsections. Calling sequences are included for these subroutines in the form of tables. The tables give a listing of the variables in the calling sequences of the subroutines along with the internal dimensions of any arrays

used as input or output by the subroutines. With one exception, these subroutines must be called directly by the flow solver. Although Subroutine NPCOUPLE is called only from Subroutine NPSOURCE, it is considered here in order to discuss the various vibrational coupling models (Sec. 2.4.2) from which the user may choose.

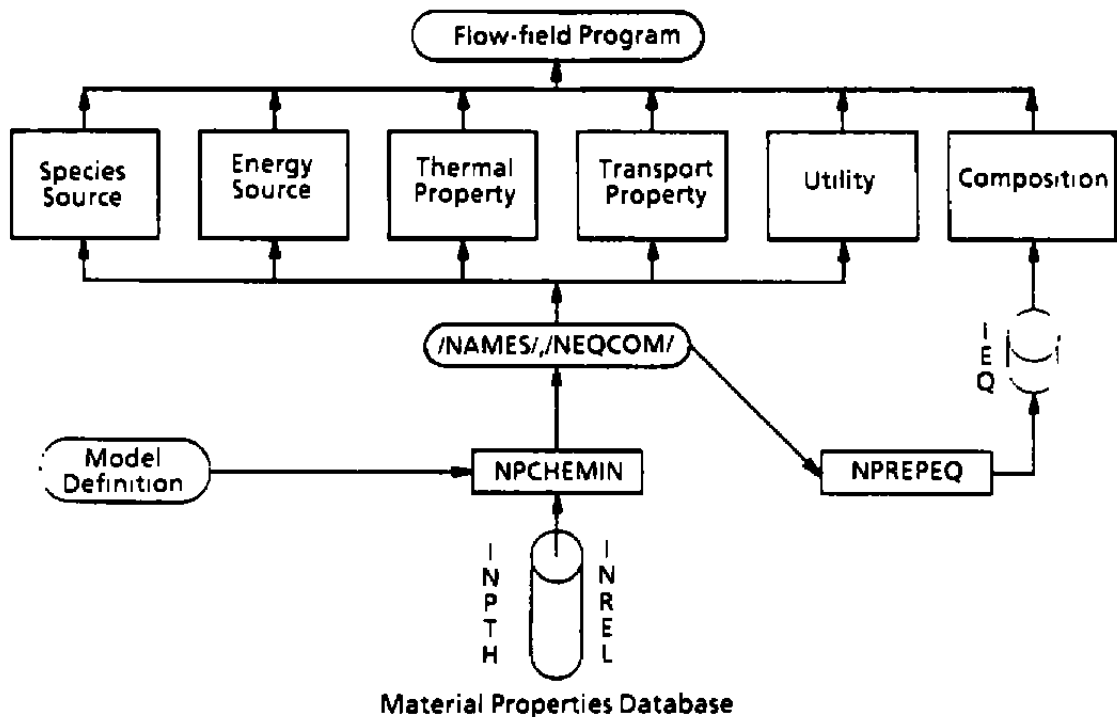


Figure 2. Schematic of NEQPAK data flow.

Table 4. Current Values of Some Important Dimensions

MXBR	Maximum number of thermofit ranges	6
MXNE	Maximum number of elements	8
MXNP	Maximum number of grid points in a vector	101
MXNR	Maximum number of reactions	50
MXNS	Maximum number of species	15
MXNV	Maximum number of oscillators	7
MXEQT	Maximum number of equilibrium temperatures	26
MXEQP	Maximum number of equilibrium pressures	26
LENGTH	Maximum record length for unit IEQ	8*(MXNS + 4)
MXNT	Maximum number of temperature types	9
MXRAD	Maximum number of radiating processes	0
MXNI	Maximum number of internal energy modes	3

3.2 SETTING UP

In the flow solver, the user must define and open the file which contains the reaction mechanism and assign it to unit number INPR, while the files which contain the material properties database must be opened and assigned to unit numbers INPTH and INREL. If some region or regions of the flow field are assumed to be in thermochemical equilibrium, the user must also open unit IEQ for direct access specifying a record length of $8 * (MXNS + 4)$ to provide access to the equilibrium composition tables described below.

The user should consider editing NPDIMEN to adjust the array dimensions for a particular problem when compiling NEQPAK. Default values for all array dimensions are listed in Table 4.

3.2.1 Input Processing

Subroutine NPCHEMIN reads the reaction file, identifies the species involved in the problem, and arranges them according to category. The free electron E^- , if present, is listed first and is followed sequentially by the other monatomic species, virtual species (identified by an asterisk), the NVIB nonequilibrium vibrators listed in the VIB array, neutral molecules, and finally ions (positively or negatively charged). Some of these categories may not exist or there may be some overlap. NPCHEMIN first identifies the species present in the current problem, and then extracts the necessary thermophysical data from the database, sets up the stoichiometric matrices relating the species to the reactions in which they appear, calculates certain species-dependent constants, and sets all the necessary flags. These data are loaded into the common block /NEQCOM/. Certain items such as species names which might be used directly by the flow code for reporting purposes are also returned through the argument list.

Communication with NPCHEMIN is through the calling sequence shown in Table 5. Note that VIB, NVIB, SPECFS, and FSCOMP are used for both input and output. Since some of the reactants may not have been input to NPCHEMIN through the SPECFS array, the number and order of the species may differ on output from their input values. The compositions in FSCOMP will be arranged to agree with the species order in SPECFS. The thermal model is selected by specifying a value for the variable MODE. MODE is set equal to 1, 2, 3, or 4, depending on which of the four thermal models described in Sec. 2.2 the user chooses.

Input of SPECFS and FSCOMP values is required only for inert species such as argon, which do not appear in the reactions being considered. Species names are character constants and must be in standard chemical notation with no internal blanks. It is best if the units of FSCOMP have "moles" or "particles" in the numerator such as $kg\text{-moles}/m^3$.

Table 5. Calling Sequence for Subroutine NPCHEMIN

SUBROUTINE NPCHEMIN(HALT,INPR,INPTH,INREL,MODE,NSFS,NSPEC,NVIB, NTMP,SPECFS,VIB,FSCOMP,WT)			
INPUT			
HALT		If TRUE, stops run if any missing data	
INPR		Reaction input unit	
INPTH		Property data input unit	
INREL		Relaxation data input unit	
MODE		Thermochemical model	
NSFS		Number of species in free-stream	
SPECFS(MXNS)		Names of free-stream species	
FSCOMP(MXNS)	γ_s	Free-stream composition	Any units
NVIB		Number of nonequilibrium vibrators	
VIB(MXNV)		Names of nonequilibrium vibrators	
OUTPUT			
SPECFS		Species considered in this run	
FSCOMP		Free stream composition of above species	
NSPEC		Length of SPECFS and FSCOMP arrays	
VIB		Nonequilibrium vibrators considered in this run	
NVIB		Length of VIB array	
NTMP		Number of temperature types considered	
WT(MXNS)	M_s	Species molecular weights	kg/kg-mole

The VIB array need only be filled if MODE = 4 is selected. In this case the user must set NVIB equal to the number of vibrators specified to be in thermal nonequilibrium and the VIB array must contain the names of the N_v vibrators specified. On output from NPCHEMIN, the user must examine the FSCOMP array to determine the order in which NEQPAK has indexed the vibrators. If MODE = 1, 2, or 3 is chosen, then all the user need do is set NVIB = 0 on input to NPCHEMIN.

Subroutine NPCHEMIN will unconditionally abort the run if it cannot find thermodynamic data for a species. However, since NEQPAK will run fairly well if transport data are missing for some species, the logical variable HALT allows the user to override program termination. The run will be terminated if any data are missing and HALT = .TRUE., while the program will continue to run if HALT = .FALSE.

In order to avoid the necessity of testing at every grid point at each entry into some subroutines for the very special case that $\gamma_s = 0$, NPCHEMIN will add 10^{-15} to all elements of the output FSCOMP array. This procedure will lead to an initial charge imbalance if electrons are involved in the chemical model and FSCOMP is expressed in mass units such as partial densities or mass fractions.

3.2.2 Equilibrium Composition Table

In reacting flow problems, it is necessary to augment the usual boundary conditions on velocity and total energy with wall boundary conditions for each species. One frequent assumption is that of a "fully catalytic" wall, i.e., that the gas is in chemical equilibrium at the wall temperature and pressure. This equilibrium composition may be calculated by minimizing the Gibbs free energy of the mixture subject to the constraints of a fixed total mass and fixed atomic mass fractions.

Since the minimization procedure is an iterative process (typically 20 to 30 cycles per case) involving the evaluation of the free energy for each of the n species and the solution of an n by $(n + 1)$ matrix equation at each cycle, the direct minimization process at a boundary point is probably equivalent in CPU time to the chemical calculations at 10 field points. The obvious way to overcome this delay is to interpolate in a table which has been specialized to a small range of temperatures and pressures typical of the problem in hand. For instance, if wall temperature is specified, then pressure would be the only independent variable.

Subroutine NPPEPEQ (Table 6) has been set up to create such a table, although it could be used one pressure-temperature point at a time. NPPEPEQ is a driver program which performs the necessary initialization, such as the calculation of the atomic mass fractions, sets up the pressure-temperature matrix, calls Subroutine NPEQLBRM to perform the free-energy minimization for each pressure-temperature point, and returns as output the calculated density, equilibrium sound speed, and equilibrium composition. Only the substances in the species list created by NPCHEMIN are considered in the minimization procedure. Species free energies are calculated by Subroutine NPGIBBS and therefore are consistent with NEQPAK thermodynamics.

A convenient way of setting up an aerodynamic calculation would call NPCHEMIN and NPPEPEQ at an early stage and use the species names output through the NPCHEMIN argument "SPECFS" to initialize the composition. A call to NP THERM (Sec. 3.6) could then give initial values for the energy variables.

3.2.3 Multiple Domains

Many aerodynamic problems involve regions of essentially different chemistry such as the core of a rocket plume or the boundary layer on an ablating or diffusion-cooled surface. Here, the user might choose to merge the applicable reaction sets and work with a large species list. Such a procedure would be wasteful of both memory and time. An alternative procedure would be to call NPCHEMIN (and NPPEPEQ if necessary) once for each reaction set, and to write the variables stored in the common blocks to separate files or logical records. Then

on crossing the boundary between flow regions, a single read statement would provide all the reaction rates and properly indexed material properties relevant to the domain. The user would still need to develop his own method to properly pass information from domain to domain as NEQPAK does not provide such a capability.

Table 6. Calling Sequence for Subroutine NPREPEQ

SUBROUTINE NPREPEQ(FSCOMP,RHOFS,T1,T2,P1,P2,NPRS,NTMP,IEQ)

Outputs the equilibrium composition at equally spaced temperatures and pressures. Subroutine NPCHEMIN must be called first to set up species property arrays.

INPUT

FSCOMP(MXNS)	—	Free-stream composition	(kg-moles/m ³)
RHOFS	—	Free-stream density	(kg/m ³)
T1,T2	—	Minimum and maximum temperature	(K)
P1,P2	—	Minimum and maximum pressure	(Pa)
NPRS	—	Number of pressures	—
NTMP	—	Number of temperatures	—
IEQ	—	Fortran unit number for output	—

NOTE

T1 may be greater or less than T2. P1 may be greater or less than P2.

3.3 CHEMICAL SOURCE TERMS

The species source terms \dot{w}_s in Eq. (3) and their derivatives with respect to the independent variables γ_s and T_q are evaluated in Subroutine NPSOURCE. The gain and loss terms, $\dot{G}_{r,s}$ and $\dot{L}_{r,s}$, defined in Sec. 2.4 are returned in addition to \dot{w}_s , since some specialized integration algorithms treat the two terms differently. The calling sequence is shown in Table 7.

Table 7. Calling Sequence for Subroutine NPSOURCE

SUBROUTINE NPSOURCE(GAM,TEMP,DERIV,LOW,NP,INC,TMIN,GAIN,LOSS,WDOT,DWDTM,DWDG)

INPUT

GAM(MXNS,NP)	γ_s	Concentration of species s at point n	(kg-moles/m ³)
TEMP(NT*NP)	T_q	Temperature of type q at point n	(K)
DERIV	—	Flag to control calculation of derivatives	—
LOW,NP,INC	—	Do-loop controls	—
TMIN	T_{min}	Minimum temperature for calculating reactions	(K)

OUTPUT

GAIN(MXNR,MXNS,NP)	$\mathcal{G}_{r,s}$	Increase of species s at n by reaction r	(kg-moles/s/m ³)
LOSS(MXNR,MXNS,NP)	$\mathcal{L}_{r,s}$	Decrease of species s at n by reaction r	(kg-moles/s/m ³)
WDOT(MXNS,NP)	\dot{w}_s	Net change of species s at point n	(kg-moles/s/m ³)
DWDTM(MXNT,MXNS,NP)	$\partial \dot{w}_s / \partial T_M$	Derivative of WDOT wrt. temperature m at n	(kg-moles/s/K/m ³)
DWDG(MXNS,MXNS,NP)	$\partial \dot{w}_s / \partial \gamma_j$	Derivative of WDOT wrt. concentration of species j at n	(s ⁻¹)

3.3.1 The TEMP Array

Both $\mathcal{L}_{r,s}$ and $\mathcal{G}_{r,s}$ involve the forward rate coefficients k_r^f defined by Eq. (28) in terms of a "generic" temperature T_q which may differ from reaction to reaction and may well be some user-defined function as discussed in Sec. 2.4 above. These chemical temperatures are supplied to NPSOURCE through the TEMP array.

TEMP is a singly-dimensioned array of length NT times NP where NT is the number of different temperatures used in a particular problem and NP is the number of grid points.

The variable NT is determined by NPCHEMIN from the input reaction data and stored in common block NEQCOM. The value of NT is returned to the flow program via the argument NTMP.

NPSOURCE evaluates the forward rate for reaction number IR at grid point IP using the temperature TEMP(IT), where

$$IT = (TTYPEF(IR)-1)*NP + IP$$

and TTYPEF(IR) and TTYPER(IR) are arrays used to store the information on which generic temperature T_q is used to evaluate the forward and backward rates. TTYPEF and TTYPER are stored in the common block /NEQCOM/ (Appendix C) and correspond to the variables TYPEF and TYPER read by NPCHEMIN from the reaction data file (Appendix F). By convention, TYPE = 1 is assigned to the translational temperature of the heavy particles and TYPE = 2 is assigned to the translational temperature of the free electron. Thus, NT is greater than or equal to 2 except for a nonionized gas in thermal equilibrium. For the two-temperature model, the vibrational temperature and the electron temperature are equal and are both assigned TYPE = 2.

The TEMP array is also used by Subroutine NPSVC (Sec. 3.4.4) when the user models vibration-chemistry-vibration coupling with one of the models described in Secs. 2.4.2 and 2.5.4. When this is the case, if Model 3 were chosen, then TYPE = 3 would correspond to T_v . If Model 4 were chosen, then TYPE = 3 through TYPE = 2 + N_v would correspond to the vibrational temperatures of the species which the user specified to be in thermal nonequilibrium. The temperatures must be entered into the TEMP array in the order in which the vibrators appear in the FSCOMP array on return from NPCHEMIN (Sec. 3.2.1). The user may wish to write a preprocessor code which calls NPCHEMIN to determine this order.

Any user-defined temperatures, such as that suggested by Park (Ref. 13) (Sec. 2.4), are the final entries into the TEMP array and would be assigned TYPE ≥ 3 .

3.3.2 Rate Coefficients

The forward reaction rate coefficient is modeled with the modified Arrhenius form, Eq. (28), namely

$$k_r^f = A_r T_q^{B_r} \exp(-C_r/T_q)$$

and T_q may be any one of the temperatures defined by the various kinetic models.

3.3.3 Calculation of Reverse Rates

The method of calculating the reverse rate for the r th reaction is communicated to NPSOURCE through the flag REV(r) which has a value of 0, 1, or 2 as determined by Subroutine NPCHEMIN from the reaction data file (see Appendix E). Unless otherwise specified, REV(r) = 1 and Eqs. (29) and (30) are applied using a G_f^0 calculated in Subroutine NPGIBBS from the polynomial fits of Eq. (30).

If REV(r) = 2, the reverse rate coefficient is calculated directly using the curve fits

$$D_r T_q^{E_r} \exp(-F_r/T_q) \quad (67)$$

which are entered for each reaction. The reverse rate is evaluated using the temperature type TTYPER(r).

If REV(r) = 0, the reverse rate is not evaluated at all. This is useful in modeling irreversible reactions such as those found in certain global combustion models.

3.3.4 Source Term Derivatives

Since the source terms in Eqs. (3) and (6) tend to be "stiff," the use of implicit methods for solving the conservation equations has become common practice. However, many algorithms for integrating "stiff" systems of differential equations require the evaluation of Jacobian derivatives. Since the evaluation of these elements is time consuming, it is sometimes advantageous to omit the re-evaluation of a Jacobian for several iteration cycles or marching steps. A common approximation in many algorithms is to use only the diagonal terms of the Jacobian, i.e., $J_{s,s} = \dot{w}_s/\gamma_s$.

The variety of possible thermodynamic models and conservation variables makes it impractical to furnish the source term derivative values in exactly the form required by each solution algorithm. Instead, NPSOURCE and all other NEQPAK source modules calculate the source term derivatives with respect to the independent variables supplied to the module. If the logical variable DERIV = .TRUE., NPSOURCE returns the derivatives $\partial \dot{w}_s / \partial \gamma_j$ and $\partial \dot{w}_s / \partial T_m$ where T_m may be any one of the temperatures in the TEMP array.

Users must then apply the chain rule to form the Jacobian elements to suit their own needs.

The derivatives which enter the Jacobian are not entirely independent. In the first place, conservation of atoms imposes N_{elts} linear constraints

$$\sum_{m=1}^{N_s} \alpha_{l,m} \dot{w}_m = 0.0, \quad l = 1, \dots, N_{elts}$$

where $\alpha_{l,m}$ is the number of atoms of element l in species m , and N_{elts} is the number of different atom types. Second, conservation of mass requires that

$$\sum_{s=1}^{N_s} \mathcal{M}_s \gamma_s = \rho, \quad (68)$$

where ρ is the ordinary global density and \mathcal{M}_s is the molecular weight of species s . Finally, if mass fractions $Y_s = \gamma_s \mathcal{M}_s / \sum_j \mathcal{M}_j \gamma_j$ or mole fractions $X_s = \gamma_s / \sum_j \gamma_j$ are used in formulating the conservation equations, then these fractions must sum to 1.0. References 14 and 47 discuss the wisdom of using the foregoing constraints to replace one or more of the species conservation equations. Since there are so many choices available, NPSOURCE evaluates the derivatives as if these constraints did not exist. However, if the reactions are input correctly, both \dot{w}_s and its derivatives will automatically satisfy the constraints. Thus, users may safely manipulate the values returned by NPSOURCE to suit their own integration strategy.

3.3.5 Vibrational Coupling

If any reaction is input with a non-zero value for the flag CTYPE(r), NPCHEMIN sets the logical variable COUPLE = .TRUE. and NPSOURCE calls Subroutine NPCOUPLE to calculate a vibrational coupling factor for the reaction. As discussed in Sec. 2.4.2, this method of modeling the effect of vibrational excitation on chemical reaction rates assumes that the quoted rate coefficients were measured for a thermal equilibrium situation and multiplies Eq. (28) by a function of translational and vibrational temperatures. NEQPAK extends this model slightly to allow separate coupling factors Ψ_f and Ψ_r for the forward and reverse directions. These coupling factors are calculated in Subroutine NPCOUPLE.

Coupling models proposed by Olynick and Hassan (Ref. 11), by Landrum and Candler (Ref. 12), and by Knab, Frühauf, and Jonas (Ref. 10) are implemented in NPCOUPLE. NPCOUPLE uses the array CTYPE(r) to determine which coupling model to apply to reaction number "r." CTYPE(r) corresponds to the variable KPL read by NPCHEMIN from the reaction data file (assigned to unit number INPR). In the reaction data file, the user should set KPL = 1 for Olynick-Hassan coupling, KPL = 2 to select the Landrum-Candler model, or KPL = 3, 4, or 5 to choose one of the coupling models developed by Knab, Frühauf, and Jonas. The user should set KPL = 0 when using the one-temperature model or when

modeling the effects of thermal nonequilibrium on reaction rates with Park's model. The other parameters needed by a particular coupling model are entered via the G, H, and U input variables. During the reaction processing performed by NPCHEMIN, the values of G, H, and U are loaded into the common arrays GK(r), HK(r), and UK(r).

CTYPE = 1: Olynick—Hassan Coupling The Olynick-Hassan coupling model was developed for dissociation reactions of the form



where molecule AB is a rotationless harmonic oscillator and M is an arbitrary third body. In their analysis, Olynick and Hassan assumed that the vibrational energy of AB is given by a Hinshelwood distribution. Since the Hinshelwood distribution does not allow for population inversions, the Olynick-Hassan model is not valid for expanding flows.

Let $z = e_{v,s}/(\mathcal{R}T_v)$ and define

$$x = (1 - T_v/T)T_{d,s}/T_v$$

where $T_{d,s}$ is the dissociation temperature of AB . Then, the forward coupling factor is

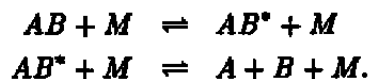
$$\Psi_f = \frac{z\Gamma(z, x)}{x^z}$$

where $\Gamma(z, x)$ is the incomplete gamma function. The reverse coupling factor is

$$\Psi_r = 1.0$$

The incomplete gamma function is evaluated by the function NPSGAM using an algorithm from Press, et al. (Ref. 27). Input of the Olynick-Hassan model into the reaction mechanism file is illustrated by the reaction set "hassan" in Appendix F-1.

CTYPE = 2: Landrum-Candler The Landrum-Candler model was developed from an intensive numerical investigation of the dissociation of N_2 . Its applicability to other diatomic species has not been investigated, so the generalization coded here may not be warranted. The essence of the model is to replace the dissociation of the diatomic molecule AB by the two-step reaction



In the above reactions, AB^* represents the AB molecules with vibrational quantum numbers $v \geq v_c = (T_{d,AB} - T)/\theta_{AB}$, where $T_{d,AB}$ is the dissociation temperature of AB , $T_{d,AB} = \Delta_{AB}/\mathcal{R}$. Based on the results of their numerical investigation, Landrum and Candler

assumed that the virtual species AB^* is in thermal equilibrium, but AB has a vibrational temperature $T_v \neq T$. Landrum and Candler argued that

$$\Psi_f = \exp(\bar{\beta}\theta_{AB} \frac{T - T_v}{T_v T}) \frac{\exp[-(v_c - 1)\theta_{AB}/T_v]}{\mathcal{Z}(v_c\theta_{AB}, T_v)}$$

for the reaction



In the definition of Ψ_f above, θ_{AB} is the characteristic vibrational temperature of AB , and \mathcal{Z} is the vibrational partition function for AB . \mathcal{Z} is computed under the assumption that the vibrational energy mode of AB is described by a harmonic oscillator truncated at quantum number $v_c - 1$. \mathcal{Z} is calculated by Subroutine NPART. The parameter $\bar{\beta} = \text{GK}(\text{IR})$ is supposed to correct for the anharmonicity of AB . Landrum and Candler were able to obtain impressive agreement with their full simulation results for N_2 by taking $\bar{\beta} = 5.0$ and increasing the Millikan-White (Ref. 28) vibrational relaxation time τ [Eq. (46)] by a factor of 25.

The reactions in Eq. (33) are entered into the reaction file in the usual way as illustrated by the reaction set "candler" shown in Appendix F-1. In the last reaction of this set, the electron temperature ($\text{TYPER} = 2$) is assumed to control the recombination of NO^+ and E^- .

NPCEMIN assigns the same thermodynamic and transport properties to the virtual molecule AB^* as to AB so it is not necessary for the user to make any special entries in the database.*

CTYPE = 3,4,5: KNAB, FRÜHAUF, and JONAS Knab, Frühauf, and Jonas (Ref. 10) have extended the concept of vibrational coupling to reaction types other than dissociation. Table 8 shows for each type of reaction the coupling factors $\Psi_f(T, T_v)$ recommended by Knab, et al. and the CTYPE values assigned to the reactions by NEQPAK.

The input parameter $\phi_r = \text{HK}(r) + \text{UK}(r) * T$ measures the probability that a molecule in vibrational state l will dissociate. If $\phi = \infty$, dissociation is equally probable from all vibrational levels. The values for HK and UK are read from the reaction mechanism file. Knab, et al. also introduce an effective activation temperature $a_r = \alpha C_r$ for reaction r . An appropriate value for α is supplied via the input variable G. If one sets $\alpha = 1$, the formulation of Eq. (37) reduces to that of Treanor and Marrone (Ref. 25).

Reaction set "fruhauf" in Appendix F-1 illustrates the input for all three reaction types listed in Table 8.

* In order to completely implement Landrum and Candler's method, the user would have to redo the curve fits for both AB and AB^* using the thermal models of the molecules defined in Ref. 12.

Table 8. Coupling Factors for Various Reaction Types

CTYPE	Reaction	Forward Rate	Reverse Rate
3	$AB + M \rightleftharpoons A + B + M$	$\Psi_4 k_r^f$	k_r'
4	$AB + C \rightleftharpoons AC + B$	$\Psi_3 k_r^f(T)$	$\Psi_5 k_r'(T)$
5	$A + B \rightleftharpoons AB^- + E^+$	$k_r^f(T)$	$\Psi_5 k_r'(T_e)$

3.4 VIBRATIONAL ENERGY SOURCE TERMS

The species vibrational energy is affected by inelastic collisions with heavy molecules and with electrons. During a heavy particle collision there may be an exchange of vibrational energy. The species vibrational energy is also affected by an increase or decrease in the number of vibrationally excited molecules through chemical reaction. These interactions are modeled by the Subroutines NPEVDOT, NPSVE, NPSVV, and NPSVC, respectively, as discussed below. Interaction with the electromagnetic field is not modeled at the present time. All inputs into the vibrational energy source term subroutines dealing with species-dependent quantities are dimensioned with the parameter MXNS and are indexed according to species number in the order returned by NPCHEMIN. On output, all arrays dealing with the vibrational energy source term and its derivatives are dimensioned with the parameter MXNV and are indexed according to vibrator number in the order in which the vibrators appear in the FSCOMP array on return from NPCHEMIN. If the logical variable DERIV = .TRUE., Subroutine NPSVC will return derivatives of $\dot{\omega}_i$ with respect to γ_s , T , and $T_{v,s}$. The other source modules will return appropriate derivatives regardless of DERIV. If Model 2 or Model 3 is chosen, $\sum_{i=1}^{N_v} \gamma_{i+N_e} \dot{\omega}_i$ and $\sum_{i=1}^{N_v} \gamma_{i+N_e} \partial \dot{\omega}_i / \partial T_v$ are returned in the positions for vibrator number 1 where N_e is the number of elements (including free electrons) present in the mixture. All the vibrational energy source term routines return the time rates of change of energy densities in terms of W/m^3 .

3.4.1 V-T Interaction

Landau and Teller (Ref. 29) showed that if the vibrational energy levels of a diatomic atom are equally spaced (harmonic oscillator assumption) and that if an inelastic collision with another atom induces only single-level transitions among the vibrational energy levels then the time rate of change of the vibrational energy as it relaxes towards equilibrium is given by

$$S_s^{v-T} = \gamma_s \frac{(e_s^{v*} - e_s^v)}{\tau_s}$$

where the e_s^{v*} is the vibrational energy computed with the translational temperature and τ_s is the so-called relaxation time. S_s^{v-T} is computed in NEQPAK in Subroutine NPEVDOT. The calling sequence for NPEVDOT is shown in Table 9. On input, NPEVDOT requires the species vibrational energies e_s^v and specific heats at constant volume $C_{v,s}^v$. When calling NPEVDOT with Model 2, the user must first call Subroutine NPTRM (Sec. 3.6) with $MODE = 3$ and $T_e = T_v$ to separate the contributions of the electron-electronic excitation energy modes from the vibrational energy modes. For all species, $e_s^v = h_s^v$ and $C_{p,s}^v$. Strictly speaking, Eq. (42) is valid only for a harmonic oscillator, but it is applied to anharmonic oscillators in Subroutine NPEVDOT by calling NPTRM to calculate the equilibrium vibrational energy e_s^{v*} .

The species relaxation time τ_s is evaluated in Subroutine NPRELAX which is called from NPEVDOT.

Subroutine NPLAXIN, which is called by NPCHEMIN, reads the necessary relaxation data from unit INREL.* If NPLAXIN does not find data for a particular interaction pair, the subroutine generates the necessary coefficients by making use of the correlation of Milliken and White, Eq. (46).

3.4.2 V-E Interaction

An encounter between a free electron and a molecule may result in the transfer of kinetic energy from the electron to a vibrational mode of the heavy particle. The probability for such an interaction is an extremely irregular function of the electron kinetic energy. Nevertheless, Lee (Refs. 8 and 30) has been able to model the process with an equation of the Landau-Teller type [Eq. (42)]

$$S_s^{v-e} = \gamma_s \frac{e_s^{v*} - e_s^v}{\tau_{e,s}}$$

where e_s^{v*} is the vibrational energy evaluated at the electron temperature and the relaxation time, $\tau_{e,s}$, is given by

$$\tau_{e,s} = \frac{2}{n_e (1 - e^{-\theta_s/T_e})^2 \int k_{0,v} v^2 dv}$$

* Provision has been made to allow NPLAXIN to read this block from a different unit from that used for the rest of the thermal properties database to allow some experimentation with relaxation rates without the risk of corrupting these data.

Table 9. Calling Sequence for Subroutine NPEVDT

SUBROUTINE NPEVDT(TT,TE,ESV,CVSV,GAM,P,LOW,NP,INC,DEVDT,EVDOTDT,EVDOTDG,EVDOTTV)

INPUT

TT(NP)	T	Translational temperature at point n	(K)
TE(NP)	T_e	Electronic temperature at n	(K)
ESV(MXNS,NP)	e_s^v	Vibrational energy of species s at n	(J/kg-mole)
CVSV(MXNS,NP)	$C_{v,s}^v$	Vibrational specific heat of species s at n	(J/kg-mole/K)
GAM(MXNS,NP)	γ_s	Concentration of species s at point n	(kg-moles/m ³)
P(NP)	p	Static pressure of the mixture at n	(Pa)
LOW,NP,INC	---	Do-loop controls	---

FROM COMMON

MODEL	2,3,4	Thermal model definition	---
-------	-------	--------------------------	-----

OUTPUT

DEVDT(MXNV,NP)	S_s^{v-T}	Time rate of change of vibrational energy of mixture or individual species at n	(W/m ³)
EVDOTDT(MXNV,NP)	$\partial S_s^{v-T} / \partial T$	Derivative of DEVDT wrt. translational temperature at n	(W/m ³ /K)
EVDOTDG(MXNV,NP)	$\partial S_s^{v-T} / \partial \gamma_j$	Derivative of DEVDT wrt. the concentration of species j at n	(W/kg-mole)
EVDOTTV(MXNV,NP)	$\partial S_s^{v-T} / \partial T_{v,s}$	Derivative of DEVDT wrt. vibrational temperature at n	(W/m ³ /K)

where n_e is the electron number density, θ_s is the characteristic vibrational temperature of species s, and $k_{0,v}$ is the rate constant for a transition from the vibrational ground state to vibrational level v.

The S_s^{v-e} terms are calculated in Subroutine NPSVE. The calling sequence for NPSVE is shown in Table 10. Subroutine NPSVE uses polynomial fits to the natural logarithm of the integral term of Eq. (49) to calculate the relaxation rate for electron impact. The rate

data from Lee (Ref. 30), Huo, et al. (Ref. 48), Kieffer (Ref. 49), and Slinker and Ali (Ref. 50) were integrated numerically and fitted at AEDC.

Table 10. Calling Sequence for Subroutine NPSVE

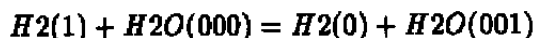
SUBROUTINE NPSVE(TE,GAM,CVSV,ESV,LOW,NP,INC,SVE,SVETE,SVEG,SVETV)

INPUT			
TE(NP)	T_e	Electronic temperature at n	(K)
GAM(MXNS,NP)	γ_s	Concentration of species s at point n	(kg-moles/m ³)
ESV(MXNS,NP)	e_s^v	Vibrational energy of species s at n	(J/kg-mole)
CVSV(MXNS,NP)	$C_{v,s}^v$	Vibrational specific heat of species s at n	(J/kg-mole/K)
LOW,NP,INC	—	Do-loop controls	—
FROM COMMON			
EVCDEF(5,MXNS)	—	Coefficients in cross-section polynomial	—
MODEL	2,3,4	Thermal model definition	—
OUTPUT			
SVE(MXNV,NP)	S_s^{v-e}	Excitation rate by electron impact at n	(W/m ³)
SVETE(MXNV,NP)	$\partial S_s^{v-e} / \partial T_e$	Derivative of SVE wrt. electronic temperature at n	(W/m ³ /K)
SVEG(MXNV,NP)	$\partial S_s^{v-e} / \partial \gamma_j$	Derivative of SVE wrt. the concentration of species j at n	(W/kg-mole)
SVETV(MXNV,NP)	$\partial S_s^{v-e} / \partial T_{v,s}$	Derivative of SVE wrt. vibrational temperature at n	(W/m ³ /K)

Since the vibrational energy gained by the molecule is lost by the electron, NPSVE should not be called for Model 2 in which vibrational and electron energy are pooled.

3.4.3 V-V Interaction

It is possible for two molecules to exchange vibrational energy during a collision, but this process is unlikely unless the molecules happen to have vibrational levels v_1 and v_2 with nearly the same energy. This vibrational exchange may be considered to be a reaction such as



which describes the interchange of vibrational energy between H2 and one of the modes of H2O. Rate data for such V-V reactions are available (Ref. 31), but considering level-to-level transitions of the kind indicated is computationally expensive. Therefore, NEQPAK has adopted the model of Candler and MacCormack (Ref. 15) in the form proposed by Knab, et al. (Ref. 10). The crude model described by Eq. (50) is evaluated in Subroutine NPSVV with the calling sequence of Table 11.

3.4.4 V-C Interactions

It is clear that the dissociation of a vibrating molecule removes its vibrational energy from the species pool and that the formation of a new molecule must add some vibrational energy to the pool. NEQPAK offers the user several models of vibration-chemistry coupling to choose from. The models are coded in Subroutine NPSVC whose calling sequence is shown in Table 12. Calls to NPSVC must be preceded by calls to NPRELAX (Table 13) and NPSOURCE. NPSOURCE must be called to obtain values for \dot{w}_s , $\mathcal{G}_{r,s}$, $\mathcal{L}_{r,s}$, and $\partial \dot{w}_s / \partial \gamma_j$, and $\partial \dot{w}_s / \partial T_m$. The call to NPRELAX is necessary to get values for τ_s , $\partial \tau_s / \partial T$, and $\partial \tau_s / \partial \gamma_j$.

Non-preferential Dissociation The simplest assumption is that the energy gained or lost during the reaction is just the average vibrational energy of the species, i.e.,

$$S_s^{v-c} = \dot{w}_s e_s^v.$$

This non-preferential dissociation assumption is appropriate for Model 2 and also for Olynick-Hassan coupling (Ref. 11)(CTYPE = 1).*

Landrum-Candler Coupling The Landrum-Candler theory (Sec. 2.4.2) assumes that vibrational levels $v < v_c$ relax according to the Landau-Teller theory but the upper vibrational levels (the virtual species AB^*) are in thermal equilibrium. The critical level is

$$v_c = \frac{\epsilon_{AB} - T}{\theta_{AB}} + 1$$

* Since all the terms needed to compute the term S_s^{v-c} defined in Eq. (51) are available by calling NPSOURCE (Sec. 3.3) and NP THERM (Sec. 3.6), users might choose to construct S_s^{v-c} and the appropriate derivatives within the flow solver as an alternative to calling NPSVC.

where ϵ_{AB} is the dissociation temperature of AB and θ_{AB} is the characteristic vibrational temperature for species AB .

Only S_s^{v-v} defined by Eq. (53) and its derivatives with respect to temperature, concentration, and vibrational energy are returned by Subroutine NPSVC. The Landau-Teller term at the beginning of Eq. (52) is calculated separately by a call to NPEVDOT (Table 9).

Table 11. Calling Sequence for Subroutine NPSVV

SUBROUTINE NPSVV(TT,GAM,EVS,CVSV,LOW,NP,INC,SVV,SVVT,SVVG,SVVTV)

INPUT			
TT(NP)	T	Translational temperature at (K) point n	
GAM(MXNS,NP)	γ_s	Concentration of species s (kg-moles/m ³) at n	
EVS(MXNS,NP)	e_s^v	Vibrational energy of (J/kg-mole) species s at n	
CVSV(MXNS,NP)	$C_{v,s}^v$	Vibrational specific heat of (J/kg-mole) species s at n	
LOW,NP,INC	—	Do-loop controls	—
FROM COMMON			
THET(MXNS)	θ_s	Characteristic vibrational (K) temperature of species s	
SLJ(MXNS,MXNS)	$\sigma_{i,j}$	Lenard-Jones collision (m) diameter	
OUTPUT			
SVV(MXNV,NP)	S_s^{v-v}	Vibrational energy source (W/m ³) term at n	
SVVT(MXNV,NP)	$\partial S_s^{v-v} / \partial T$	Derivative of SVV wrt. (W/m ³ /K) translational temperature at n	
SVVG(MXNV,MXNS,NP)	$\partial S_s^{v-v} / \partial \gamma_j$	Derivative of SVV wrt. (W/kg-mole) concentration of species j	
SVVTV(MXNV,MXNV,NP)	$\partial S_s^{v-v} / \partial T_{v,j}$	Derivative of SVV wrt. (W/m ³ /K) vibrational temperature of species j	

KFJ Coupling The coupling theory of Knab, et al. (Ref. 10) is invoked for reactions with CTYPE = 3,4,5. Unlike the other coupling theories described above, in the KFJ theory (Ref.

10) the vibrational coupling factor depends on both the translational and the species vibrational temperatures. Thus, NPSVC returns S_g^{v-c} along with its derivatives with respect to translational temperature, species concentrations, and species vibrational temperatures when KFJ coupling is invoked.

Table 12. Calling Sequence for Subroutine NPSVC

NPSVC(TEMP,GAM,GAIN,LOSS,WDOT,EVS,CVSV,TAU,DWDG,DWDTH,DTAUT,DTAUG,DERIV,LOW,NP,INC,SVC,SVCT,SVCG)

INPUT

TEMP(NT*NP)	T_q	Temperature of type q at point n	(K)
GAM(MXNS,NP)	γ_s	Concentration of species s at point n	(kg-moles/ m^3)
GAIN(MXNR,MXNS,NP)	$G_{r,s}$	Increase of species s at n by reaction r	(kg-moles/ s/m^3)
LOSS(MXNR,MXNS,NP)	$L_{r,s}$	Decrease of species s at n by reaction r	(kg-moles/ s/m^3)
WDOT(MXNS,NP)	\dot{w}_s	Net change of species s at point n	(kg-moles/ s/m^3)
EVS(MXNS,NP)	e_s^v	Vibrational energy of species s	(J/ m^3)
CVSV(MXNS,NP)	e_s^v	Vibrational heat capacity of species s	(J/(m^3K))
LOW,NP,INC	—	Do-loop controls	—
TAU(MXNS,NP)	τ_s	Relaxation time of species s at n	(s)
DTAUT(MXNS,NP)	$\partial\tau_s/\partial T$	Derivative of TAU with respect to translational temperature at n	(s/K)
DTAUG(MXNS,MXNS,NP)	$\partial\tau_s/\partial\gamma_j$	Derivative of TAU with respect to concentration of species j at n	($s-m^3/kg-mole$)
DWDG(MXNS,MXNS,NP)	$\partial\dot{w}_s/\partial\gamma_j$	Derivative of WDOT with respect to concentration of species j at n	(s^{-1})
DWDTH(MXNT,MXNS,NP)	$\partial\dot{w}_s/\partial T_m$	Derivative of WDOT with respect to temperature of type m	(kg-moles/ $s/m^3/K$)

Table 12. Calling Sequence for Subroutine NPSVC (Concluded)

FROM COMMON			
THET(MXNS)	θ_s	Characteristic vibrational temperature	(K)
DISOC(MXNS)	Δ_s	Dissociation energy of species s	(J/kg-mole)
CK(MXNR)	C_r	Activation energy of reaction r	(K)
GK,HK,UK(MXNR)	—	Parameters for reaction r	—
CTYPE(MXNR)	—	Coupling type for reaction r	—
NC	—	Maximum value of ctype	—
NT	—	Number of temperature types	—
OUTPUT			
DERIV	—	Flag to control calculation of derivatives	—
SVC(MXNV,NP)	S_n^{v-c}	Rate of increase of vibrational energy	(J/s/m ³)
SVCT(MXNV,NP)	$\partial S_n^{v-c} / \partial T_m$	Derivative of SVC wrt temperature m	(W/m ³ /K)
SVCG(MXNV,MXNS,NP)	$\partial S_n^{v-c} / \partial \gamma_j$	Derivative of SVC wrt concentration of species j	(W/kg-mole)

Table 13. Calling Sequence for Subroutine NPRELAX

SUBROUTINE NPRELAX(TT,GAM,P,LOW,NP,INC,TAU,DTAUT,DTAUG)

INPUT			
TT(NP)	T	Translational temperature at (K) point n	
GAM(MXNS,NP)	γ_s	Concentration of species s (kg-moles/m ³) at point n	
P(NP)	p	Pressure at n (Pa)	
LOW,NP,INC	—	Do-loop controls —	
OUTPUT			
TAU(MXNS,NP)	τ_s	Relaxation time of species s (s) at n	
DTAUT(MXNS,NP)	$\partial\tau_s/\partial T$	Derivative of TAU wrt to (s/K) translational temperature at n	
DTAUG(MXNS,MXNS,NP)	$\partial\tau_s/\partial\gamma_j$	Derivative of TAU with (s-m ³ /kg-mole) respect to concentration of species j at n	

3.5 ELECTRON-ELECTRONIC ENERGY SOURCE TERMS

The energy of the free electron is affected by elastic and inelastic collisions with heavy particles, by electron production, by interaction with applied and induced electric fields, and by radiation processes. The energy of electronic excitation may be lost to radiation. Of these effects, only those dealing with collisions and electron production through chemical reaction are included with the NEQPAK source terms [$\dot{\omega}'$ of Eq. (6)]. Each of the source terms discussed in Sec. 2.6 is calculated in a separate module, but a single call to Subroutine NPEEDOT (Table 14) will return $\dot{\omega}_e^e$ defined in Eq. (9). NPEEDOT also returns the derivatives of $\dot{\omega}_e^e$ with respect to translational and electron-electronic temperatures in the array EEDOTTM. The derivatives with respect to translational temperature are stored as TYPE = 1 while the derivatives with respect to electron temperature are stored in the slot for TYPE = 2. NPEEDOT also returns the derivative of $\dot{\omega}_e^e$ with respect to species concentrations. The user should call NPEEDOT even for Model 2.

The constants ξ_1 , ξ_2 , and ξ_3 in Eqs. (58) to (60) are set by NPCHEMIN. The effective cross section σ in Eq. (57) is computed in Subroutine NPSEET with quadratic fits taken from Ref. 9.

The energy lost by the free electron in exciting vibration is calculated in Subroutine NPSVE (Table 10). As discussed in Sec. 2.5.2, NPEEDOT will not call NPSVE when the vibrational and electron-electronic energies are pooled (Model 2).

The stoichiometric product in Eq. (61) is evaluated in NPCHEMIN and a logical variable, IMPACT, is set to .TRUE. if the product equals 1.

3.6 THERMAL PROPERTIES

Dimensional values ($J/kg\text{-mole}$ or $J/kg\text{-mole}/K$) for the enthalpy and constant pressure molar heat capacity of the individual species are obtained by calling Subroutine NPTHERM using the calling sequence of Table 15.

For the one-temperature model (Model 1), NPTABLE calculates the dimensionless heat capacity and dimensionless enthalpy for each species using the polynomial curve fits of Eqs. (62)–(64).

Table 14. Calling Sequence for Subroutine NPEEDOT

NPEEDOT(TT,TE,GAM,EVS,CVSV,LOW,NP,INC,DERIV,EEDOT,EEDOTTH,EEDOTG)

INPUT			
TT(NP)	T	Translational temperature at point n	(K)
TE(NP)	T_e	Electron-electronic temperature	(K)
GAM(MXNS,NP)	γ_s	Concentration of species s at n	(kg-moles/m ³)
EVS(MXNS,NP)	e_s^v	Vibrational energy of species s at n	(J/kg-mole)
CVSV(MXNS,NP)	$C_{v,s}^v$	Vibrational specific heat of species s at n	(J/kg-mole/K)
LOW,NP,INC	—	Do-loop controls	—
DERIV	—	Flag to control calculation of derivatives	—
FROM COMMON			
NT	—	Number of temperature types	—
NS	—	Number of species	—
NV	—	Number of nonequilibrium vibrators	—
NE	—	Number of elements	—
OUTPUT			
EEDOT(NP)	$\dot{\omega}_e^e$	Rate of change of electronic energy	(W/m ³)
EEDOTTH(MXNT,NP)	$\partial \dot{\omega}_e^e / \partial T_m$	Derivative of EEDOT wrt. temperature of type m	(W/m ³ /K)
EEDOTG(MXNS,NP)	$\partial \dot{\omega}_e^e / \partial \gamma_s$	Derivative of EEDOT wrt. concentration of species s	(W/kg-mole)

Table 15. Calling Sequence for Subroutine NP THERM

SUBROUTINE NP THERM(TT,TV,TE,LOW,NP,INC,MODE,HS,HSV,HSE,CPS,CPSV,CPSE)

INPUT			
TT(NP)	T	Translational temperature at point n	(K)
TV(MXNV,NP)	$T_{v,s}$	Vibrational temperature of species s	(K)
TE(NP)	T_e	Electron-electronic temperature at n	(K)
LOW,NP,INC	—	Do-loop controls	—
MODE	1,2,3,4	Thermal model definition (Sec. 2.2)	—
FROM COMMON			
NS	—	Number of species	—
NV	—	Number of vibrators	—
OUTPUT			
HS(MXNS,NP)	h_s	Total species enthalpy (MODEL=1) Translation-rotation part (MODEL>1)	(J/kg-mole)
HSV(MXNS,NP)	h_s^v	Vibrational part of species energy Includes electron contribution (MODEL=2)	(J/kg-mole)
HSE(MXNS,NP)	h_s^e	Electronic part of species enthalpy	(J/kg-mole)
CPS(MXNS,NP)	$C_{p,s}$	Species molar heat capacity (MODEL=1) Translation-rotation part (MODEL>1)	(J/kg-mole/K)
CPSV(MXNS,NP)	$C_{p,s}^v$	Vibrational part of specific heat	(J/kg-mole/K)
CPSE(MXNS,NP)	$C_{p,s}^e$	Electronic part of specific heat	(J/kg-mole/K)

NOTES

1. Kinetic energy of the electron is listed as a vibration-electronic energy for MODEL=2 and as electronic excitation energy for MODEL=3 or MODEL=4.
2. Enthalpy and energy of internal modes are equal.

Table 16. Calling Sequence for Subroutine NPEFINDT

SUBROUTINE NPEFINDT(E,GAM,WHICH,LOW,NP,INC,T)			
INPUT			
E(NP)	e^m	Mixture energy of type m	(J/m ³)
GAM(MXNS,NP)	γ_s	Concentration of species s	(kg-moles/m ³)
WHICH	—	Flag to select which temperature is to be calculated	—
LOW,NP,INC	—	Do-loop controls	—
T(NP)	T_m	Initial guess for the temperature	(K)
FROM COMMON			
NS	—	Number of species	—
NV	—	Number of nonequilibrium vibrators	—
MODEL	1,2,3,4	Thermal model definition (Sec. 2.2)	—
IONIZED	—	If .TRUE., mixture is ionized.	—
HFO(MXNS)	h_s^0	Heat of formation of species s at 0° K	(J/kg-mole)
ETHROT(MXNS)	—	Number of translation-rotation modes	—
OUTPUT			
T(NP)	T_m	Converged value of temperature of type WHICH	(K)

NOTE

For MODEL=2, use WHICH =2 for vibrational electronic temperature. For MODEL=3, use WHICH =2 for electron-electronic temperature and WHICH =3 for vibrational temperature.

In a multitemperature thermal model, it is necessary to separate the contributions of the internal modes to the species enthalpy and heat capacity. This separation, which is performed by Subroutine NP THERM, is possible since translation and rotation (assumed fully excited) contribute a constant $3.5\mathcal{R}$ to the heat capacity. If the two-temperature model (Model 2) is selected, the vibrational portions of the enthalpy and specific heat, h_s^V and $C_{p,s}^V$, for molecular species s are calculated by first computing h_s and $C_{p,s}$ from the curve fits using T_v and then subtracting $3.5\mathcal{R}T_v$ and $3.5\mathcal{R}$, respectively. The heat of formation, $h_{0,s}^0$, is also subtracted from $h_{v,s}$. Next, h_s^{tr} and $C_{p,s}^{tr}$ are simply set equal to $3.5\mathcal{R}T$ and $3.5\mathcal{R}$ for diatomic species and $2.5\mathcal{R}T$ and $2.5\mathcal{R}$ for monatomic species. In both cases, the heat of formation is included with h_s^{tr} . If the gas is ionized, NP THERM sets h_e^V and $C_{p,e}^V$ equal to $2.5\mathcal{R}T_v$ and $2.5\mathcal{R}$. If a separate electron temperature is assumed (Model ≥ 3), the procedure is to evaluate h_s and C_p from the curve fits at T_v and the electronic contribution is calculated using T_v in Subroutine NPEL PART. Next, h_s^v and $C_{p,s}^v$ are corrected as described above to get the proper vibrational contributions. The translation-rotation part and the electronic part are then evaluated at the appropriate temperatures and returned in separate arrays.

The contributions of the bound electronic states to the species heat capacity and enthalpy are (Ref. 36)

$$C_{p,s}^e = \frac{\sum_{l=1}^{NLEV_s} (\psi_l)^2 \exp(-\psi_l)}{Z} - \left[\frac{1}{Z} \sum_{l=1}^{NLEV_s} \psi_l \exp(-\psi_l) \right]^2 \quad (69)$$

$$h_s^e = \frac{1}{Z} \sum_{l=1}^{NLEV_s} \psi_l \exp(-\psi_l), \quad (70)$$

where $\Psi_l \equiv \xi_l/kT$. The electronic partition function is

$$Z \equiv \sum_{l=1}^{NLEV_s} g_l \exp(-\psi_l);$$

where $NLEV_s$ is the number of electronic energy levels for species s , g_l is the degeneracy of the l th electronic level, and ξ_l is its energy.

3.6.1 Temperature Calculations

Since the energy and heat capacity are, in general, nonlinear functions of temperature, an iterative procedure is necessary to determine the temperature from the energy or enthalpy. Subroutines NPEFINDT and NPHFINDT are provided for the calculation of temperature from the mixture energy density E and mixture enthalpy density H in J/m^3 , respectively. The calling sequence for Subroutine NPEFINDT is shown in Table 16. The use of NPHFINDT

is identical except that the input is enthalpy per unit volume of the mixture rather than thermal energy density. Since Newton's method is used for the iteration, convergence is generally rapid, especially when the initial temperature estimate is good. The number of iterations is currently limited to ten.

3.6.2 Entropy

Some reacting gas codes (especially those which assume equilibrium chemistry) use entropy as a variable. Subroutine NPENTRPY can be used to calculate the species and the mixture entropy for a given translational temperature. The calling sequence is shown in Table 17.

Table 17. Calling Sequence for Subroutine NPENTRPY

SUBROUTINE NPENTRPY(TT,LOW,NP,INC,CHI,S,SNIX)			
INPUT			
TT(NP)	T	Translational temperature array	(K)
LOW, NP, INC	—	Do-loop controls	—
CHI(MINS, NP)	χ_s	Mole fraction of species s	—
OUTPUT			
S(MINS, NP)	—	Dimensionless entropy of species s	—
SNIX(NP)	γ	Entropy of mixture	(J/kg-mole/K)

3.7 TRANSPORT PROPERTIES

The coefficients of viscosity which enter the right-hand side of the momentum conservation equations, Eq. (4), and the thermal conductivities which enter the energy conservation equations, Eqs. (5) and (6), are calculated by calling Subroutine NPTRANS (Table 18). In order to keep NPTRANS applicable to any thermal model, a generalized internal heat capacity CPI and a corresponding internal thermal conductivity TKI, as in Eq. (23), have been introduced. Subroutine NPRETRN acts as a translator between the notation of NP THERM and that of NPTRANS. Since it is a translator, it must be called between NP THERM and NPTRANS. NPRETRN determines the number of internal energy storage modes, NI, from the thermal model and the number of nonequilibrium vibrators N_v , and copies the heat capacities output by NP THERM into the array CPI. Subroutine NPRETRN as written assumes that the temperature of the free electron is equal to that of the electronic states. As the number

and sophistication of thermal models increase, this subroutine will need to be rewritten. Usage of NPRETRN is detailed in Table 19.

If the gas is not ionized, the effective diffusion coefficients which are returned by NPTRANS can be used in Fick's law, Eq. (15), to calculate the species diffusion velocities. If there is only one heavy ion, the user should employ the species mobilities returned by NPTRANS to calculate the ambipolar diffusion coefficient D_a defined by Eq. (21) for use as the effective diffusion coefficient in Fick's law. If there is more than one heavy ion in the chemical model, Subroutine NPOLAR (Table 20) must be called to evaluate the species diffusion velocities.

3.7.1 Transport Properties of Pure Species

As written, Eq. (22) is applicable to a single-temperature thermal model (Model 1). For multi-temperature thermal models (Model > 1), a separate coefficient

$$\lambda_s^m = \rho D_{s,e} \frac{C_{p,s}^m}{M_s}$$

defined in Eq. (23) is calculated for each nonequilibrium mode.

Note that the transport properties of the heavy species are evaluated with the translational temperature and that η_e and λ_e are evaluated with the translational temperature of the free electron T_e . For Model 1, the user must set $T_e = T$.

The curve-fit coefficients $b_{i,s}$ and $d_{i,s}$ in Eqs. (65) and (66) for the eleven air species have been adapted from Ref. 42. Low-temperature curve-fit coefficients for species other than the components of heated air have been obtained from a variety of sources (Refs. 19 and 41).

3.7.2 Mixture Transport Properties

The overall viscosity of the mixture is calculated by the semi-empirical method of Armaly and Sutton (Ref. 22). A similar approximation, also due to Armaly and Sutton (Ref. 23), is used to obtain the individual parts of the mixture thermal conductivity, λ_{mix}^m , for Model < 4. The methods proposed by Armaly and Sutton were adopted in NEQPAK because when NEQPAK was under development they were the only models available that specifically took ionization into account. When $T_{internal}$ varies from species to species (Model 4), it is impractical to define a mixture conductivity for that particular internal energy mode. Hence, for Model 4, the contributions of species vibrational modes are returned as separate entries in the TKI array.

Table 18. Calling Sequence for Subroutine NPTRANS

SUBROUTINE NPTRANS(LOW,NP,INC,TT,TE,CPT,CPI,GAM,D,VIS,MOB,TKT,TKI,TKE)

INPUT			
LOW,NP,INC	—	Do-loop controls	—
TT(NP)	T	Heavy particle translational temperature (K)	
TE(NP)	T_e	Electron translational temperature (K)	
CPT(MXNS,NP)	$C_{p,s}$	Species translational heat capacity or total heat capacity (MODEL= 1)	(J/kg-mole/K)
CPI(MXNI,MXNS,NP)	$C_{p,s}^m$	Species internal heat capacity	(J/kg-mole/K)
GAM(MXNS,NP)	γ_s	Concentration of species s	(kg-moles/m ³)
FROM COMMON			
NI	—	Number of nonequilibrium internal energy modes	—
MODEL	1,2,3,4	Thermal model definition (Sec. 2.2)	—
OUTPUT			
D(MXNS,NP)	D_s	Effective species diffusivity	(m ² /s)
MOB(MXNS,NP)	μ_s	Ion mobility	(m ² /s/volt)
VIS(NP)	η	Mixture viscosity	(N-s/m ²)
TKT(NP)	λ	Thermal conductivity of mixture (MODEL=1) or frozen mixture conductivity (MODEL > 1)	(W/m/K)
TKI(MXNI,NP)	λ^i	Internal conductivity of mixture	(W/m/K)
TKE(NP)	λ_e	Thermal conductivity of electrons	(W/m/K)

Table 19. Calling Sequence for Subroutine NPRETRN

SUBROUTINE NPRETRN(CPS,CPSV,CPSE,LOW,NP,INC,CPT,CPI)

INPUT			
CPS(MXNS,NP)	$C_{p,s}$	Species heat capacity	(J/kg-mole/K)
CPSV(MXNS,NP)	$C_{p,s}^v$	Vibrational heat capacity of species s	(J/kg-mole/K)
CPSE(MXNS,NP)	$C_{p,s}^e$	Species electronic heat capacity	(J/kg-mole/K)
LOW,NP,INC	—	Do-loop controls	—
OUTPUT			
CPT(MXNS,NP)	$C_{p,s}$	Translational or total heat capacity of species s	(J/kg-mole/K)
CPI(MXNI,MXNS,NP)	$C_{p,s}^m$	Internal heat capacity of mode m of species s	(J/kg-mole/K)
TO COMMON			
NI	—	Number of nonequilibrium internal energy modes	—

Table 20. Calling Sequence for Subroutine NPOLAR

SUBROUTINE NPOLAR(GAM,D,MU,G,LOW,NP,INC,V)

INPUT			
GAM(MXNS,NP)	γ_s	Concentration of species s	(kg-moles/m ³)
D(MXNS,NP)	D_s	Effective diffusion coefficient of species s	(m ² /s)
MU(MXNS,NP)	μ_s	Mobility of species s	(m ² /volt/s)
G(MXNS,NP)	$\nabla\chi_s$	Gradient of mole-fraction of species s	(m ⁻¹)
LOW,NP,INC	—	Do-loop controls	—
FROM COMMON			
ALPIJ(MXNE,MXNS)	$\alpha_{i,j}$	Number of atoms of kind "i" in species "j"	—
OUTPUT			
V(MXNS,NP)	u_s	Diffusion velocity of species s	(kg-moles/m ³)

3.8 UTILITY ROUTINES

NEQPAK provides two utility routines, NPFRCON and NPTOCON (Tables 21 and 22) to convert composition units to and from the $kg\text{-moles}/m^3$ used in the computational modules. Subroutine NPWEIGHT (Table 23) calculates the molecular weight of the mixture.

Table 21. Calling Sequence for Subroutine NPFRCON

SUBROUTINE NPFRCON(ARRAY,LOW,WP,INC,TO,DENS,WT,OUT)

This subroutine converts composition or rate units from $kg\text{-moles}/m^3$ to the units specified by the character variable TO.

INPUT

ARRAY(MXNS,NP)	—	Array of compositions or rates	—
LOW,WP,INC	—	Do-loop controls	—
TO	—	Units of "OUT". Use 'mole/mole', 'gram/gram', 'mole/gram' or 'gram/cu.m'. Enclose in single quotes(')	—
DENS(NP)	ρ	Mixture mass density	(kg/m^3)
WT(NP)	\mathcal{M}	Mixture molecular weight	($kg/kg\text{-mole}$)

OUTPUT

OUT(WP)	—	Output array	—
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Table 22. Calling Sequence for Subroutine NPTOCON

SUBROUTINE NPTOCON(ARRAY,LOW,NP,INC,FROM,DENS,WT,OUT)

This subroutine converts composition or rate units from the units specified by the character variable FROM to kg-moles/m³.

INPUT			
ARRAY(MXNS,NP)	—	Array of compositions or rates	—
LOW,NP,INC	—	Do-loop controls	—
FROM	—	Units of "ARRAY". Use 'mole/mole', 'gram/gram', 'mole/gram', 'gram/cu.m', 'mole-fraction' or 'mass-fraction'. Use lower case and enclose in single quotes(')	—
DENS(NP)	ρ	Mixture mass density	(kg/m ³)
WT(NP)	\mathcal{M}	Mixture molecular weight	(kg/kg-mole)
FROM COMMON			
EMI(MXNS)	\mathcal{M}_s	Species molecular weight	(kg/kg-mole)
OUTPUT			
OUT(NP)	γ_s	Output array	(kg-mole/m ³)

Table 23. Calling Sequence for Subroutine NPWEIGHT

SUBROUTINE NPWEIGHT(C,LOW,NP,INC,UNITS,WT)			
INPUT			
C(MXNS,NP)	γ_s	Array of compositions	—
LOW,NP,INC	—	Do-loop controls	—
UNITS	—	Units of "C". Use 'mole/mole', 'gram/gram', 'mole/gram', 'gram/cu.m'. Use lower case and enclose in single quotes(')	—
OUTPUT			
WT(NP)	M	Mixture molecular weight	(kg/kg-mole)

3.9 EQUILIBRIUM COMPOSITION

Interpolation for a particular temperature and pressure within the table of equilibrium compositions prepared by Subroutine NPREPEQ (Table 6) is performed by Subroutine NPEQCOMP (Table 24). Note that Fortran unit IEQ must have been opened as a direct access device before calling NPEQCOMP for the first time. The record length is 8*(MXNS + 4).

Table 24. Calling Sequence for Subroutine NPEQCOMP

SUBROUTINE NPEQCOMP(TWALL,PWALL,IEQ,OUT)

INPUT			
TWALL	—	Temperature	(K)
PWALL	—	Pressure	(Pa)
IEQ	—	Fortran unit number for input	—
FROM COMMON			
NEQT	—	Number of equilibrium temperatures	—
NEQP	—	Number of equilibrium pressures	—
DELT	—	Temperature increment	(K)
DELP	—	Pressure increment	(Pa)
OUTPUT			
OUT(MXNS+2)	—	Output array	—

NOTE

The first element of the OUT array contains the density of the mixture in kg/m^3 , while the second element contains the mixture frozen sound speed in m/s . The remaining N_s positions are filled with the species concentrations in $kg - moles/m^3$. The compositions are listed in the order in which they are returned in the FSCOMP array by Subroutine NPCHEMIN (Sec. 3.2.1).

4.0 CONCLUDING REMARKS

NEQPAK is a set of Fortran 77 routines and databases which are useful in the development and application of both reacting flow solvers and static kinetics programs. It is unique in its inclusion of thermal nonequilibrium effects and in the range of its databases.

- The thermal properties database covers the range from 100 to 35,000 K.
- The transport properties database extends from 300 to 30,000 K.
- Ambipolar diffusion effects may be evaluated.
- The effects of thermal nonequilibrium on the thermal conductivity may also be evaluated.
- A utility for correlating user-supplied reaction data with the material properties databases is provided.
- The interactions between vibrational and chemical relaxation may be investigated by using multiple-temperature reaction models or by application of coupling factors suggested by contemporary theories.
- A module for calculating the equilibrium chemical composition as a function of pressure and temperature is also included. This module may be of use in initializing flow calculations or in evaluating solid surface boundary conditions.

The modularity and flexibility of NEQPAK invite extension of its capabilities in many directions. The most pressing and practicable enhancements are

- extension of the transport database to the very low temperatures encountered in wind tunnel testing,
- the development of a surface chemistry capability, and
- the capability to calculate the energy lost through equilibrium radiation.

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APPENDIX A

SPECIES EQUATION WITH AMBIPOLAR DIFFUSION

This appendix derives the form, Eq. (18), of the species conservation equation which applies to a plasma containing several positively and negatively charged ionic species. In the following derivation, $\Gamma = \sum_i \gamma_i$ and all summations have the limits 1 and N_s .

Substitution of Eq. (7.3-27) into Eq. (7.4-3) of Ref. 7 and neglect of the thermal and pressure diffusion terms yields the following equation for the diffusive mass flux, which appears on the right-hand side of Eq. (3).

$$\rho \gamma_s \vec{u}_s = \Gamma^2 \sum_{i=1}^{N_s} m_i D_{si} [\nabla \chi_i - \frac{\gamma_i m_i}{p} (\frac{\vec{F}_i}{m_i} - \rho \sum_k \gamma_k \vec{F}_k)] \quad (\text{A-1})$$

The units in Eq. (A-1) are consistent ($\text{kg-mole-m}^2/\text{s}$) if \vec{F} is a force per kg-mole and the units of the multicomponent diffusion coefficient D_{si} are m^2/s . Note that $D_{si} = \mathcal{D}_{si}$ only if $N_s = 2$. Let

$$\vec{F}_s = -\alpha_{e,s} N e \vec{E} \quad (\text{A-2})$$

where e is the elementary charge, \vec{E} is the electric field strength (N/C) and N is Avogadro's number. The number of electrons per particle of species s is $\alpha_{e,s}$. Note that α for a positive ion is negative since one or more electrons have been removed. Substitution of Eq. (A-2) into the flux equation, Eq. (A-1), yields

$$\rho \gamma_s \vec{u}_s = \Gamma^2 \sum_j m_j D_{s,j} [\nabla \chi_j + \frac{\gamma_j m_j e N}{p \rho} (\frac{\rho \alpha_{e,j}}{m_j} - \sum_k \gamma_k \alpha_{e,k}) \vec{E}] \quad (\text{A-3})$$

From Eq. (A-3) it is clear that the diffusive flux contains a term, known as the "drift velocity," which is proportional to the electric field strength \vec{E} . The constant of proportionality is known as the "ion mobility," μ_j . For a neutral plasma, $\sum_k \alpha_{e,k} n_k = 0$ and

$$\gamma_s \vec{u}_s = \frac{\Gamma^2}{\rho} \sum_j m_j D_{s,j} [\nabla \chi_j + \frac{e N}{p} \gamma_j \alpha_{e,j} \vec{E}] \quad (\text{A-4})$$

It was shown in Table 1 of Sec. 2.3 that in the absence of ionization, Fick's law

$$\gamma_s \vec{u}_s = -\Gamma D_s \nabla \chi_s \quad (\text{A-5})$$

is a good approximation to Eq. (A-1) if the effective diffusion coefficient D_s is appropriately defined. Now, if it is assumed that the right-hand side of Eq. (A-5) continues to be a reasonable approximation to the first term of Eq. (A-4), even in the presence of an electric field, and an ion mobility is defined as

$$\mu_s \equiv \frac{\Gamma^2 e \mathcal{N} \sum_j m_j D_{s,j} \alpha_{e,j}}{p \rho \gamma_s \alpha_{e,s}} \quad (\text{A-6})$$

then the species conservation equations become

$$\frac{\partial \gamma_s}{\partial t} + \nabla \cdot (\gamma_s \vec{U}) = \dot{w}_s + \nabla \cdot [\Gamma D_s \nabla \chi_s - \alpha_{e,s} \mu_s \gamma_s \vec{E}] \quad (\text{A-7})$$

Equation (A-7) is still general. To specialize Eq. (A-7) for ambipolar diffusion, multiply both sides by $\alpha_{e,s}$ and sum over s . The result is

$$\frac{\partial (\sum_s \alpha_{e,s} \gamma_s)}{\partial t} + \nabla \cdot (\vec{U} \sum_s \alpha_{e,s} \gamma_s) = \sum_s \alpha_{e,s} \dot{w}_s + \nabla \cdot [\Gamma \sum_s \alpha_{e,s} D_s \nabla \chi_s - \sum_s \alpha_{e,s}^2 \mu_s \gamma_s \vec{E}] \quad (\text{A-8})$$

Conservation of charge requires that

$$\sum_{s=1}^{N_s} \alpha_{e,s} \dot{w}_s = 0 \quad (\text{A-9})$$

Since the plasma is neutral,

$$\sum_{s=1}^{N_s} \alpha_{e,s} \gamma_s = 0 \quad (\text{A-10})$$

Then Eq. (A-8) becomes

$$\nabla \cdot [\Gamma \sum_s \alpha_{e,s} \gamma_s D_s \nabla \chi_s - \sum_s \alpha_{e,s}^2 \mu_s \gamma_s \vec{E}] = 0 \quad (\text{A-11})$$

In general, the electric field has both applied and induced components, $\vec{E} = \vec{E}_a + \vec{E}_i$. If there is no applied field, i.e., \vec{E} is entirely due to the equilibrium between the electrostatic and collision forces, then

$$\vec{E}_i = \frac{\Gamma}{\sigma} \sum_s \alpha_{e,s} D_s \nabla \chi_s \quad (\text{A-12})$$

where

$$\sigma \equiv \sum_s \alpha_{e,s}^2 \mu_s \gamma_s \quad (\text{A-13})$$

When $\vec{E} = \vec{E}_i$, defined by Eq. (A-12), is substituted into Eq. (A-7), the ambipolar species equation, Eq. (18), is recovered, namely

$$\frac{\partial \gamma_s}{\partial t} + \nabla \cdot (\gamma_s \vec{U}) = \dot{w}_s + \nabla \cdot [\Gamma (D_s \nabla \chi_s - \frac{\alpha_{e,s} \mu_s \gamma_s}{\sigma} \sum_j \alpha_{e,j} D_j \nabla \chi_j)] \quad (\text{A-14})$$

APPENDIX B

NONEQUILIBRIUM THERMAL CONDUCTIVITY

Kinetic theory attempts to calculate the effect of intermolecular collisions on the distribution of molecular population. The formulae usually quoted for thermal conductivity apply only to monatomic particles and must somehow be corrected for the effects of internal energy. While there are formal treatments for polyatomic molecules, the formulae are cumbersome and are also restricted to thermal equilibrium and by various assumptions about relaxation rates. Therefore, most authors simply apply some version of the Eucken correction. The following analysis follows that in Hirschfelder, Curtiss, and Bird (Ref. 7, pp. 498-501) with some slight changes in notation. A chemically pure polyatomic gas with a set of internal quantum numbers $\{i\}$ is assumed. The essential step in the following treatment is the assumption that each possible quantum state of the gas constitutes a separate species. Thus, the single polyatomic gas is replaced, in thought, with a mixture of monatomic species to which the results of ordinary kinetic theory apply.

One of the general results of the Chapman-Cowling-Enskog (Ref. 7) solution of the Boltzmann equation is that the flux of energy across some reference surface is

$$\bar{q} = -\lambda^0 \nabla T + \sum_i n_i (5kT/2 + e_i) \bar{u}_i \quad (\text{B-1})$$

where e_i is the energy per molecule of the quantum state i and

$$\lambda^0 = 5\eta \bar{C}_V / 2 = (15k/4m)\eta$$

is the thermal conductivity due to translation. The viscosity is η , the mass of the molecule is m , and n_i is the number density of the molecules which are in the i th quantum state. The quantities $n = \sum_i n_i$ and $X_i = n_i/n$ are also used.

It is a good approximation that the diffusion velocity is independent of the internal quantum state. Then, since the masses of all these species are the same, the diffusion velocity of species i is

$$\bar{u}_i = -\chi_i^{-1} \mathcal{D} \nabla \chi_i \quad (\text{B-2})$$

where \mathcal{D} is the self-diffusion coefficient. It is possible to rewrite Eq. (B-1) as

$$\bar{q} = -\lambda^0 \nabla T + 2.5kT \sum_i n_i \bar{u}_i + \sum_i n_i e_i \bar{u}_i \quad (\text{B-3})$$

Since the masses of all the excited species are equal, the definition of diffusion velocity implies that $\sum_i n_i m_i \bar{u}_i = 0 = \sum_i n_i \bar{u}_i$ in this case. Substitution of Eq. (B-2) into Eq. (B-3) yields

$$\vec{q} = -\lambda^0 \nabla T - \sum_i n_i e_i \chi_i^{-1} \mathcal{D} \nabla \chi_i \quad (\text{B-4})$$

Equation (B-4) is valid for both thermal equilibrium and thermal nonequilibrium. For thermal equilibrium, the distribution of population among the internal states is Maxwellian with T as the temperature parameter. Since the temperature is now defined, application of the chain rule for derivatives and recognition that e_i is a function only of i yield

$$\vec{q} = -\lambda_0 \nabla T - n \mathcal{D} \sum_i e_i \frac{d\chi_i}{dT} \nabla T = -\lambda_0 \nabla T - n \mathcal{D} \sum_i C_V^i \nabla T_0 \quad (\text{B-5})$$

in which $C_V^i = e_i d\chi_i/dT$ is the heat capacity of the i th species. Equation (B-5) is obtained by defining $C_p = \sum_i C_V^i + \mathcal{R}$ and recognizing that the C_p returned by Subroutine NPHERM contains a contribution $3\mathcal{R}T/2$ from the translational motion which is included in the λ_0 term and a contribution $\mathcal{R}T$ from the pV -work part of the enthalpy.

In a multitemperature model, it is assumed that the first l_r quantum states correspond to rotation with a Boltzmann temperature T_r , that states $l_r < i \leq l_v$ correspond to vibration and are distributed according to T_v , while the remaining states $l_v < i \leq l_e$ correspond to electronic excitation with a Boltzmann temperature T_e . The energy flux can then be written

$$\vec{q} = -\lambda_0 \nabla T - n \mathcal{D} \left[\sum_{i=1}^{l_r} C_V^i \nabla T_r + \dots \right] = -\lambda_0 \nabla T - \sum_l \lambda^l \nabla T_l$$

where $\lambda^l = n \mathcal{D} C_V^l$ is the thermal conductivity of the l th internal mode.

APPENDIX C **VARIABLES IN COMMON BLOCK NEQCOM**

<u>Variable</u>	<u>Type</u>	<u>Definition</u>
ALPIJ(MXNE,MXNS)	R	Number of atoms of element i in species j
AK(MXNR),...,CK(MXNR)	R	Parameters in forward reaction rate $A_r T^{B_r} \exp(-C_r/T)$, Eq. (28)
DK(MXNR),...,FK(MXNR)	R	Parameters in reverse reaction rate $D_r T^{E_r} \exp(-F_r/T)$, Eq. (67)
GK(MXNR),...,UK(MXNR)	R	Parameters in Sec. 3.3.5
B(MXNS,MXNS)	R	Constant set in NPVISCIN. Used in NPSUTTON
CHI1,CHI2,CHI3	R	Parameters ξ_1, \dots, ξ_3 in Sec. 3.5
CONTK(MXNS,MXNS)	R	Constant defined in NPVISCIN. Used in NPSUTTON
CONV(MXNS,MXNS)	R	Constant defined in NPVISCIN. Used in NPARMALY
COUPLE	L	Switch used in NPSOURCE to call NPCOUPLE
CTYPE(MXNR)	I	Coupling type for reaction r, Sec.3.3.5
C1D,...,C5D(MXNS,MXNS)	R	Coefficients of polynomial fit to binary diffusivity
DEGEN(7,MXNS)	R	Degeneracy of electronic energy level
DISOC(MXNS)	R	Dissociation energy
EFF(MXNS,MXNR)	R	Catalytic efficiency
ELEV(7,MXNS)	R	Energy of electronic level
EMI(MXNS)	R	Species molecular weight
EMIQ(MXNS)	R	Fourth root of species molecular weight
ETNROT(MXNS)	R	Dimensionless enthalpy of rigid rotator
EVCOEF(5,MXNS)	R	Fit coefficients used in NPSVE
HFO(MXNS)	R	Heat of formation
IMPACT(MXNR)	I	Marker for impact ionization reaction
ION(MXNS)	R	Ionization energy of species
IONIZED	L	Flags an ionized mixture
LINK(MXNS)	I	Links virtual molecule to real counterpart. Used in NPCOUPLE.
LION	I	Number of heavy ions
METHOD	L	Used in NPSOURCE to call NPGIBBS
MODEL	I	Distinguishes thermodynamic models
NC	I	Maximum value of CTYPE(IR)
NE	I	Number of elements
NI	I	Number of internal energy modes. Used in NPTRANS
NR	I	Number of reactions
NS	I	Number of species
NT	I	Number of temperature types
NTBR(MXNS)	I	Number of thermo-fit polynomials
NTHD	I	Number of three-body reactions
NU(MXNR)	R	Change in number of moles in reaction IR
NUP(MXNR,MXNS)	I	Stoichiometric coefficient of product
NUR(MXNR,MXNS)	I	Stoichiometric coefficient of reactant

REV(MXNR)	I	Flags method for computing reverse reaction rate
SIGMA(3,MXNS)	R	Fit coefficients used in NPSEET
SLJ(MXNS,MXNS)	R	Lenard-Jones collision diameter
SUA(MXNS)	R	Constant in Sutherland viscosity formula
SUBB(MXNS)	R	Constant in Sutherland viscosity formula
TAB(7,MXBR,MXNS)	R	Thermo-fit coefficient
TAUCON(4,MXNS,MXNS)	R	Coefficients of relaxation time fit
TBR(MXNS,MXBR)	R	Break point between thermo-fit segments
THET(MXNS)	R	Characteristic temperature for vibration
TTYPEF(MXNR)	I	Temperature type in forward direction, Sec. 3.3.1
TTYPER(MXNR)	I	Temperature type for reverse direction
ZERO(MXNS,MXNS)	R	Is zero on diagonal and one elsewhere
ZROT(MXNS)	R	rotational collision number

APPENDIX D

NEQPAK MODULES

All of the NEQPAK modules are listed in Table D-1 below. Those subroutines which must be called by the user are marked by the word "FLOW" in the "Called by" column. The calling sequence of these modules is presented in the text in the indicated tables.

Table D-1. NEQPAK Modules

Module	Called by	Function	Table
gamln	gser,gcf	helps calculate incomplete gamma function	5
gcf	npsgam	helps calculate incomplete gamma function	
gser	npsgam	helps calculate incomplete gamma function	
ltrim	npchemin	length of character string with trailing blanks removed	
nparmaly	npdiffin	returns mixture viscosity	
npart	nptrans	returns partition function of harmonic oscillator truncated at energy "a"	
nparta	npcouple	derivative of npart with respect to truncation energy	
npartt	npvc	derivative of npart with respect to temperature	
npchemin	npcouple	chemistry input	
npcopy	FLOW	copies species data	
npcouple	npchemin	returns vibrational coupling factor	
npcphs	npsource	returns specific heat and enthalpy	
npdiffin	npeqlbrm	selects diffusion data	
npeedot	npchemin	electron energy source term	14
npefindt	FLOW	finds temperature for a given energy	16
npelpart	nptherm	energy in electronic states	17
npentrp	FLOW	returns species entropy	
npeqcomp	FLOW	interpolates in composition table	24
npeqlbrm	nprepeq	returns equilibrium composition for one p,T	9
npevdot	FLOW	vibrational energy source term	
npfrcon	FLOW	converts composition variables	
npgauss	npeqlbrm	inverts matrix	21

Table D-1. NEQPAK Modules (Concluded)

Module	Called by	Function	Table
np Gibbs	np source	returns Gibbs free energy	
np hfindt	FLOW	finds temperature for a given enthalpy	
np lxin	np chemin	sets data for relaxation time	
np matrix	np eqlbrm	sets up composition matrix	
np nopref		returns $\sum_s \dot{w}_s e_{v,s}$	
npolar	FLOW	ambipolar ion diffusion velocity	20
np relax	np evdot	returns vibrational relaxation time	13
	FLOW		
np repeq	FLOW	driver for chemical equilibrium calculation	6
np retrn	FLOW	sets up call to nptrans	19
np sec	np edot	loss of energy by electron impact	
np seet	np edot	electron energy exchange by elastic collision	
np seten	np repeq	initializes composition for np eqlbrm	
np sgam	np couple	returns incomplete gamma function	
np source	FLOW	species source term	7
np sutton	nptrans	returns mixture thermal conductivity	
np svc	FLOW	effect of chemistry on vibrational energy	12
np sve	FLOW	excitation of vibration by electron	10
	np edot		
np svv	FLOW	vibration-vibration exchange	11
np table	np therm	dimensionless enthalpy and C_p for species s	
	np findt		
np therm	FLOW	enthalpy and C_p for species	15
np tocon	FLOW	composition variables to concentration	22
np trans	FLOW	returns transport properties of mixture	18
np viscin	np chemin	sets up viscosity data	
np weight	FLOW	calculates mixture molecular weight	23

APPENDIX E

ENTERING REACTION DATA

All reaction data are list directed input and are read by Fortran unit INPR. Data items are separated by commas. Omitted items are represented by commas. Items following a slash "/" will not be read.

The first record of unit INPR is used to specify the input units of the rate coefficients and the name of the reaction set, "RNAME". Use "cu.m/kmol", "c.cm.mole", "c.cm/part", or "cu.m/part" in lower case letters as shown to designate the units. The default option is "c.cm/mole".

For each reaction there is a principal record which defines the reaction and identifies the temperature functions to be used in the forward (TYPEF) and the reverse (TYPER) directions and also identifies the coupling model (KPL). The six dummy variables *A*, ..., *F* describe the temperature dependence of the forward and reverse rates as described in Secs. 3.3.2 and 3.3.3. The meaning of the parameters *G*, *H*, and *U*, which describe the effect of nonequilibrium vibration on the reaction, depends on the value of KPL as described in Sec. 3.3.5. The format for this principal record is

REACTION,TYPEF,TYPER,KPL,A,B,C,D,E,F,G,H,U

where *REACTION* is defined as CHARACTER*63. TYPEF and TYPER are integers. Species names are limited to eight characters, must begin with an alphabetic character, may not contain embedded blanks, and are delimited with spaces. NEQPAK will stop and print an error message if a species name cannot be found in the thermochemical database. Species names in the current database contain only upper case letters. An irreversible reaction is indicated by using a minus sign "-" in place of the "=" as a separator between reactants and products.

The activation temperature C_r in the argument of the exponent is a positive number corresponding to Eq. (28). Care must be taken when using published tabulations of reaction rates as there is no universally accepted standard for units or for the sign of C_r , and some authors are careless about stating their conventions.

For three-body reactions, indicated by the appearance of the character "M" among the reactants, an auxiliary record is used to input catalytic efficiencies. The format of the auxiliary record is

(*OBJECT(N),VALUE(N),N = 1,MXNS*),

where *OBJECT* is defined to be CHARACTER*8, *VALUE* is a real number, and MXNS is the maximum number of species (currently 20) set by the PARAMETER statement in file NPDIMEN.

A typical three-body reaction might be entered

```
'O2 + M = O + O + M',1,1,0,3.61E18,-1.0,59400.,3.01E15,-0.5/
'O2',9.,'O',25.,'N2',2.0,'NO+',0.0,'E-',0.0/
```

Note that stoichiometric coefficients are not entered, that the letter "M" represents any third body and causes the auxiliary record to be read, and that the rate-controlling temperature is specified by the TYPEF value of one — usually the translational temperature. Furthermore, the reaction is reversible since the separator between reactants and products is an "=" sign. Also, *D* and *E* ≠ 0.0 so that REV(r), Sec. 3.3.3, is set automatically = 2. The auxiliary fields specify catalytic efficiencies $\phi_{s,r}$ of 25.0 for oxygen atoms, 9.0 for oxygen molecules O_2 , and 2.0 for nitrogen molecules N_2 . All other species have $\phi = 1.0$ except the ions NO^+ and E^- which do not affect the reaction.

Photochemical reactions may be specified by entering the character string "HNU" as either a product or a reactant. The *OBJECT* and *VALUE* entries on the auxiliary record then represent an identifier for the photon and its wavelength, respectively. Needless to say, this identifier must be listed as a species in the thermal properties database.

As long as the rate equation fits into the Arrhenius form, Subroutine NPSOURCE will return appropriate gain and loss terms. Since photochemical reactions are often essentially irreversible, the user must take great care to ensure mass balance in setting up the reaction model. NEQPAK has no mechanism for checking this balance, nor does it possess a procedure for handling the radiant energy.

APPENDIX F

REACTION SET EXAMPLES

The first three reaction sets shown below were prepared to serve as examples in Sec. 3.3.5. They are basically the same as the Blottner set, except for specifying the indicated coupling and using the electronic temperature where appropriate. These reaction sets were not necessarily used by the indicated authors. The remaining data sets have been translated to NEQPAK notation and set up as Model 1 cases. The hydrogen-air example is taken from Ref. 52.

F-1. PURE AIR EXAMPLES

'c.cm/mole,hassan' / (Ref. 11)

```
'O2 + M = O + O + M',1,1,1,3.61E18,-1.0,59400.,3.01E15,-0.5/
'NO+',0.0,'E-',0.0,'O2',9.,'O',25.,'N2',2.0/
'N2 + M = N + N + M',1,1,1,1.92E17,-0.5,1.131E5,1.09E16,-0.5/
'N',0.0,'NO+',0.0,'E-',0.0,'N2',2.5/
'N2 + N = N + N + N',1,1,1,4.15E22,-1.5,1.131E5,2.32E21,-1.5/
'NO + M = N + O + M',1,1,1,3.97E20,-1.5,7.56E4,1.01E20,-1.5/
'NO+',0.0,'E-',0.0,'O',20.,'N',20.,'NO',20./
'NO + O = O2 + N',1,1,0,3.18E9,1.0,1.97E4,9.63E11,0.5,3600./
'N2 + O = NO + N',1,1,0,6.75E13,0.0,3.75E4,1.5E13,0.00,0.0/
'N + O = NO+ + E-',1,2,0,9.03E9,0.5,3.24E4,1.8E19,-1.0,0.0/
'END '
```

'c.cm/mole,candler' / (Ref. 12)

```
'O2 + M = O + O + M',1,1,0,3.61E18,-1.0,59400.,3.01E15,-0.5/
'O2',9.,'O',25.,'N2',2.0/
'N2 + M = N2* + M',1,1,2,8.25E16,0.0,25289.,0.,0.,0.,5.0,0.35/
'N',0.0,/
'N2 + N = N2* + N',1,1,2,6.028E16,0.,0.,0.,0.,0.,5.0,0.35/
'N2* + M = N + N + M',1,1,0,1.52E21,-1.51,13121.,0.,0.,0.,5.0,0.35/
'N',0.0/
'N2* + N = N + N + N',1,1,0,6.75E21,-1.51,13121.,0.,0.,0.,5.0,0.35/
'NO + M = N + O + M',1,1,0,3.97E20,-1.5,7.56E4,1.01E20,-1.5/
'O',20.,'N',20.,'NO',20./
'NO + O = O2 + N',1,1,0,3.18E9,1.0,1.97E4,9.63E11,0.5,3600./
'N2 + O = NO + N',1,1,0,6.75E13,0.0,3.75E4,1.5E13,0.00,0.0/
'N + O = NO+ + E-',1,2,0,9.03E9,0.5,3.24E4,1.8E19,-1.0,0.0/
'END '
```


'c.cm/mole,fruhauf' (Ref. 10)

```

'O2 + M = O + O + M',1,1,4,3.61E18,-1.0,59400.,3.01E15,-0.5,,0.7,14875.0/
'NO+',0.0,'E-',0.0,'O2',9.,'O',25.,'N2',2.0/
'N2 + M = N + N + M',1,1,4,1.92E17,-0.5,1.131E5,1.09E16,-0.5,,0.7,28275./
'N',0.0,'NO+',0.0,'E-',0.0,'N2',2.5/
'N2 + N = N + N + N ',1,1,0,4.15E22,-1.5,1.131E5,2.32E21,-1.5/
'NO + M = N + O +M',1,1,0,3.97E20,-1.5,7.56E4,1.01E20,-1.5/
'NO+',0.0,'E-',0.0,'O',20.,'N',20.,'NO',20./
'NO + O = O2 + N',1,1,3,3.18E9,1.0,1.97E4,9.63E11,0.5,3600.,0.7,18875./
'N2 + O = NO + N',1,1,3,6.75E13,0.0,3.75E4,1.5E13,0.0,0.7,9400./
'N + O = NO+ + E-',1,2,5,9.03E9,0.5,3.24E4,1.8E19,-1.0,0.0,0.7,8.1E3/
'END '

```

'c.cm/mole,blottner' (Ref. 51)

```

'O2 + M = O + O + M',1,1,0,3.61E18,-1.0,5940.0,,3.01E15,-0.5/
'NO+',0.0,'E-',0.0/
'N2 + M = N + N + M',1,1,0,1.92E17,-0.5,1.131E5,,1.09E16,-0.5,/
'N',0.0,'NO+',0.0,'E-',0.0 /
'N2 + N = N + N + N ',1,1,0,4.15E22,-1.5,1.131E5,,2.32E21,-1.5/
'NO + M = N + O +M',1,1,0,3.97E20,-1.5,7.56E4,,1.01E20,-1.5/
'NO+',0.0,'E-',0.0/
'NO + O = O2 + N',1,1,0,3.18E9,1.0,1.97E4,,9.63E11,0.5,3600/
'N2 + O = NO + N ',1,1,0,6.7513,0.0,3.75E4,,1.5E13/
'N + O = NO+ + E-',1,1,0,9.03E9,0.5,,3.24E4,,1.8E19,-1.0/
'END' /

```

'c.cm/mole,gupta' (Ref. 42)

```

'O2 + M = O + O + M',1,1,0,3.61E18,-1.0,5940.0,,3.01E15,-0.5/
'NO+',0.0,'E-',0.0/
'N2 + M = N + N + M',1,1,0,1.92E17,-0.5,1.131E5,,1.09E16,-0.5,/
'N',0.0,'NO+',0.0,'E-',0.0 /
'N2 + N = N + N + N ',1,1,0,4.15E22,-1.5,1.131E5,,2.32E21,-1.5/
'NO + M = N + O + M ',1,1,0,3.97E20,-1.5,7.56E4,,1.01E20,-1.5/
'NO+',0.0,'E-',0.0/
'NO + O = O2 + N ',1,1,0,3.18E9,1.0,1.97E4,,9.63E11,0.5,3600/
'N2 + O = NO + N ',1,1,0,6.7513,0.0,3.75E4,,1.5E13/
'N + O = NO+ + E- ',1,1,0,9.03E9,0.5,,3.24E4,,1.8E19,-1.0/
'O + E- = O+ + E- + E- ',1,1,0,3.6E31,-2.91,1.58E5,,2.2E40,-4.5 /
'N + E- = N+ + E- + E- ',1,1,0,1.1E32,-3.14,1.69E5,,2.2E40,-4.5/
'O + O = O2+ + E- ',1,1,0,1.6E17,-.98,8.08E4,,8.02E21,-1.5/
'O + O2+ = O2 + O+ ',,2.92E18,-1.11,2.8E4,,7.8E11,0.5/
'N2 + N+ = N2+ + N ',1,1,0,2.02E11,0.81,1.3E4,,7.8E11,0.5/
'N + N = N2+ + E- ',1,1,0,1.4E13,0.0,6.78E4,,1.5E22,-1.5
'O2 + N2 = NO + NO+ + E- ',1,1,0,1.38E20,-1.84,1.41E5,,1.0E24,-2.5/
'NO + O2= NO+ + E- + O2 ',1,1,0,2.2E15,-0.35,1.08E5,,2.2E26,-2.5/
'NO + N2= NO+ + E- + N2 ',1,1,0,2.2E15,-0.35,1.08E5,,2.2E26,-2.5/
'O + NO+ = NO + O+ ',1,1,0,3.63E15,-0.6,5.08E4,,1.5E13/
'N2 + O+ = O + N2+ ',3.4E19,-2.0,-2.3E4,,2.48E19,-2.2/
'N + NO+ = NO + N+ ',1.0E19,-0.93,6.1E4,,4.8E14/
'O2 + NO+ = NO + O2+ ',1.8E15,0.17,3.3E4,,1.8E13,0.5/
'O + NO+= O2 + N+ ',1,1,0,1.34E13,0.31,7.727E4,,1.0E14/
'END '/

```

F-2. HYDROGEN AIR COMBUSTION

'c.cm/mole,jachimowski'/(Ref. 52)

```

'H2 + O2 = OH + OH ',1,1,0,1.7E13,,24170./
'OH + H2 = H2O + H ',1,1,0,2.2E13,,2593./
'H + O2 = OH + H ',1,1,0,2.2E14,,8459./
'O + H2 = OH + H ',1,1,0,1.8E10,1.0,4481./
'OH + OH = H2O + O ',1,1,0,6.3E12,, 549./
'H + OH + M = H2O + M ',1,1,0,2.2E22,-2.0/
'H2O',6.0/
'H + O + M = OH + M ',1,1,0,6.0E16,-0.6/
'H2O',5.0/
'H + H + M = H2 + M ',1,1,0,6.40E17,-1.0/
'H2',2.0,'H2O',6.0/
'H + O2 + M = HO2 + M ',1,1,0,1.7E15,, -503./
'H2',2.0,'H2O',16.0/
'HO2 + H = H2 + O2 ',1,1,0,1.3E13,/
'HO2 + H = OH + OH ',1,1,0,1.4E14,,544./
'HO2 + O = OH + O2 ',1,1,0,1.50E13,0.0,478./
'HO2 + OH = H2O + O2 ',1,1,0,8.0E12,/
'HO2 + HO2 = H2O2 + O2 ',1,1,0,2.0E12/
'H + H2O2 = H2 + HO2',1,1,0,1.4E12,,1813./
'O + H2O2 = OH + HO2 ',1,1,0,1.4E13,,3222./
'OH + H2O2 = H2O + HO2 ',1,1,0,6.1E12,,720./
'M + H2O2 = OH + OH + M ',1,1,0,1.2E17,,22910./
'H2O',15.0/
'O + O + M = O2 + M ',1,1,0,6.0E13,, -503./
/
'N + N + M = N2 + M ',1,1,0,2.8E17,-0.75/
/
'N + O2 = NO + O ',1,1,0,6.4E9,1.0,3172./
'N + NO = N2 + O ',1,1,0,1.6E13/
'N + OH = NO + H ',1,1,0,6.3E11,0.5/
'H + NO + M = HNO + M ',1,1,0,5.4E15,, -302./
/
'H + HNO = NO + H2 ',1,1,0,4.8E12/
'O + HNO = NO + H2O ',1,1,0,5.0E11,0.5/
'OH + HNO = NO + H2O ',1,1,0,3.6E13/
'HO2 + HNO = NO + H2O2 ',1,1,0,2.0E12/
'HO2 + NO = NO2 + OH ',1,1,0,3.43E12,, -131./
'H + NO2 = NO + OH ',1,1,0,3.5E14,,755./
'O + NO2 = NO + O2 ',1,1,0,1.0E13,,302./
'M + NO2 = NO + O + M ',1,1,0,1.16E16,,33230./
/
'END'/

```

APPENDIX G

THE DATABASE FORMAT

Apart from the first record, which is used to identify its source and date, the material properties database is divided into four blocks which are read by Subroutines NPCHEMIN, NPDIFFIN, NPVISCIN, and NPLAXIN, respectively. Table G-1 is an excerpt from the thermochemical section showing the data for N₂. The first line of this block, which is read with the format

Table G-1. Thermochemical Data for N₂

N2	N	2.	0.	0.	0.	28.0134	2	4
3.35324E+03			.97590E+01	.15510E+02	.75	E-19	.55000E-23	-1.0 E-28
3.62100E-10	4.0		-15.40393	-.14374E-06	.75216E-15	-.14186E-23	.90669E-33	
6	300.0	1000.0	6000.0	15000.0	25000.0	30000.0		
0.34999E+01	.10160E-04							.30894E+01
0.36748E+01	-.12081E-02	.23240E-05	-.63218E-09	-.22577E-12	-17.17441		.23583E+01	
0.28963E+01	.15155E-02	-.57235E-06	.99807E-10	-.65224E-14	138.1293		.61615E+01	
0.37270E+01	.46840E-03	-.11400E-06	.11540E-10	-.32930E-15	32.47182		.13128E+01	
0.96377E+01	-.25728E-02	.33020E-06	-.14315E-10	.20333E-15	51.19068		-.37586E+02	
-.51681E+01	.23337E-02	-.12953E-06	.27872E-11	-.21360E-16	52.96151		.66217E+02	
1.0	3.0	6.0	6.0					
0.0	.592568+09	.70954E+09	.71042E+09					

(1x,a8,2x,4(a3,f3.0),f8.4,3i5), starts with the name of the substance and its chemical formula. Provision is made for four element names. Also on the first line are the species molecular weight (*kg/kg-mole*), the number of rotational degrees of freedom, and the number of electronic energy levels (NLEV). On the second line, which is read with format (1x,7e11.5), are values for the characteristic vibrational energy θ (K), for the standard heat of formation (*J/kg-mole*) at 0.0 K and 1 atm, for the dissociation energy, and for the ionization potential (both in eV). The remaining three numbers on this line are constants in a polynomial fit to the electron-neutral energy exchange cross-section. On the third line are values for the Lenard-Jones collision diameter, the rotational collision number, and fit coefficients for the electronic-vibrational energy relaxation time. The number of thermo-fit segments (NRNGE) and the junction temperatures are on the next line. The values of the seven thermo-fit coefficients for each range fill the next NRNGE lines. The last two lines of data for a species are the electronic level degeneracies and corresponding energies in *J/kg-mole*, respectively.

The boundary between the thermodynamic data and the diffusion data is marked by a line with the single entry END.

An excerpt from the diffusion database which is read by Subroutine NPDIFFIN is shown in Table G-2. This block gives, for each species, the constants necessary to calculate, from Eq. (66), the binary diffusion coefficient with the other named species. These constants are listed in inverse order, that is, the coefficient of the highest power of $\ln T$ is listed first and the constant term last. In order to assure completeness, the symmetry condition $\mathcal{D}_{i,j} = \mathcal{D}_{j,i}$ is enforced. The diffusion data for different species are separated by a line with the single entry LAST while the boundary between the diffusion data and the viscosity data is marked by a line with the single entry END.

The first few lines of the viscosity data, which are read by NPVISCIN, are shown in Table G-3. The viscosity block begins with a single line containing the number of species for which data are available. The following data are read with the format from the second line. There are two lines of data for each species: on the first line, the species name is followed by an integer, IONIN, which connects a molecule or atom with the ionized form of the same species. For instance, IONIN = 4 for NO and -4 for NO+. These links are used in setting the species parameters for use by NPSUTTON. As with the diffusion data, the fit coefficients on the second line are listed in inverse order from their use in Eq. (65). The last two entries in each line are the constants in the Sutherland viscosity expression and are no longer used.

The boundary between the viscosity data and the relaxation data is marked by a line with the single entry END.

The final block of data in the material properties database, as described in Sec. 3.4.1, is read by Subroutine NPLAXIN and consists of the parameters $\tau_{aua}, \dots, \tau_{aud}$ in Eq. (43) of Sec. 2.5.1, namely

$$p\tau_{\tau}(j,k) = \tau_{aua} T^{**} \tau_{aub} \exp(\tau_{auc}/T^{**} \tau_{aud})$$

for the relaxation time of species j in a bath of species k . As shown in Table G-4, there is one line for each pair of species.

Table G-2. Binary Diffusion Data for CO

CO					
H2	-0.491000E-02	0.143632E+00	-0.157448E+01	0.932089E+01	-0.236352E+02
O2	-0.280961E-02	0.889657E-01	-0.105720E+01	0.724306E+01	-0.220271E+02
N2	-0.292013E-02	0.915470E-01	-0.107718E+01	0.729354E+01	-0.220264E+02
H	-0.412427E-02	0.133344E+00	-0.161427E+01	0.103288E+02	-0.265753E+02
O	-0.334505E-02	0.102934E+00	-0.118857E+01	0.775935E+01	-0.222797E+02
N	-0.300961E-02	0.926432E-01	-0.107007E+01	0.715205E+01	-0.212231E+02
OH	-0.329578E-02	0.101480E+00	-0.117253E+01	0.768092E+01	-0.221562E+02
HO2	-0.281176E-02	0.890325E-01	-0.105797E+01	0.724703E+01	-0.220419E+02
H2O	0.368373E-03	0.728311E-02	-0.323631E+00	0.468910E+01	-0.194570E+02
NO	-0.292217E-02	0.916079E-01	-0.107787E+01	0.729693E+01	-0.220496E+02
AR	-0.301056E-02	0.960765E-01	-0.115119E+01	0.779324E+01	-0.232613E+02
CO	-0.293217E-02	0.919203E-01	-0.108155E+01	0.731631E+01	-0.220796E+02
CO2	-0.237574E-02	0.813037E-01	-0.104026E+01	0.755574E+01	-0.236811E+02
CN	-0.279938E-02	0.866140E-01	-0.100572E+01	0.684965E+01	-0.210421E+02
HCN	-0.974226E-03	0.448550E-01	-0.708852E+00	0.638614E+01	-0.225367E+02
N2O	-0.243124E-02	0.825726E-01	-0.104943E+01	0.757232E+01	-0.236628E+02
NO2	-0.287875E-02	0.945216E-01	-0.116502E+01	0.804363E+01	-0.242275E+02
C	-0.310294E-02	0.954079E-01	-0.110070E+01	0.730243E+01	-0.214453E+02
C2	-0.293334E-02	0.919424E-01	-0.108161E+01	0.731552E+01	-0.220272E+02
LAST					

Table G-3. Viscosity Data

41							
(7E10.4)							
O2	1						
0.0000		0.00	0.0484	-0.1455	-8.9231	1.4584E-6	110.33
N2	2						
0.00		0.0	0.0203	.4329	-11.8153	1.4584E-6	110.33
N	5						
0.00		0.0	0.0120	0.5930	-12.3805	1.4584E-6	110.33
O	3						
0.00		0.00	0.0205	0.4257	-11.5803	1.5884E-6	110.33
NO	4						
0.00		0.00000	0.0452	-0.0609	-9.4596	1.4584E-6	110.33
NO+	-4						
0.0913		-3.3178	45.1426	-270.3958	586.3300	1.4584E-6	110.33

Table G-4. Vibrational Relaxation Rate Coefficients

'N2', 'N2', 1.6909E-11, 0.0, 220.0, 0.333
 'CO', 'AR', 1.5985E-11, 0.0, 213., 0.333
 'CO', 'CO', 6.2397E-11, 0.0, 175., 0.333
 'CO', 'HE', 1.3127E-09, 0.0, 99.0, 0.333
 'CO', 'H2', 3.0959E-09, 0.0, 68.0, 0.333
 'O2', 'AR', 6.0211E-11, 0.0, 165., 0.333
 'O2', 'O2', 2.0872E-10, 0.0, 129., 0.333
 'O2', 'HE', 2.5162E-09, 0.0, 67.0, 0.333
 'O2', 'H2', 4.7853E-09, 0.0, 42.0, 0.333
 'F2', 'F3', 1.3069E-09, 0.0, 65.0, 0.333
 'CL2', 'CL2', 1.1968E-09, 0.0, 58., 0.333
 'BR2', 'BR2', 1.1625E-09, 0.0, 48., 0.333
 'I2', 'I2', 2.3233E-09, 0.0, 127.0, 0.333
 'NO', 'NO', 7.0219E-11, 0.0, 168.0, 0.333

APPENDIX H

TABULATED SPECIES

The material properties database currently contains data for the species listed in Table H-1.

Table H-1. Tabulated Species

E-	C	H	N	O
AR	C2	H2	N+	O+
AR+	C2-	H2O	N2	O-
	C3	H2O+	N2+	O2
	CH	H2O2	N2O	O2+
	CH2	H3+	NCO	O2-
	CH2O	HCN	NH	OH
	CH2OH	HCO	NH3	OH+
	CH3	HCO+	NO	OH-
	CH3OH	HE	NO+	
	CH4	HE+	NO2	
	CN	HNCO		
	CO	HNO		
	CO+	HO2		
	CO2			

APPENDIX I

A TYPICAL APPLICATION

A typical application of NEQPAK to a hypothetical problem is outlined below. There are, of course, many flow problems, both internal and external, for which an understanding of thermochemical effects is important. There are also many flow solvers now available. In order to be concrete, a particular class of problem and a particular computational approach will be assumed. Only the procedures which involve the chemistry or thermophysical properties will be discussed.

The problem to be solved is that of determining the electromagnetic properties of the plasma about a reentry body. An iterated implicit flow code with shock fitting is used. The reaction set "blottner" from Appendix F-1 and thermal equilibrium are selected.

- **PRELIMINARIES**

- Choose values for INPR, INREL, and INPTH which will not interfere with other input-output units needed by the code.

- Open INPR, INREL, and INPTH to read formatted files.

- Set maximum array dimensions by editing file NPDIMEN (Table 4).

- **INPUT**

- Set NSFS = 2; SPECFS(1) = O2, SPECFS(2) = N2,
CON(1) = .22, CON(2) = .78

- Set MODEL = 1, NVIB = 0, VIB = dummy, HALT = .FALSE.

- CALL NPCHEMIN(.....) (Table 5).

- After return from NPCHEMIN:

- *SPECFS(1) = E-, CON(1) = 1.0E-15

- *SPECFS(2) = O, CON(2) = 1.0E-15

- *SPECFS(3) = N, CON(3) = 1.0E-15

- *SPECFS(4) = O2, CON(4) = 0.22

- *SPECFS(5) = N2, CON(5) = 0.78

- *SPECFS(6) = NO + , CON(6) = 1.0E-15

- *SPECFS(7) = NO, CON(7) = 1.0E-15

- *NSPEC = 7

- *NTMP = 1

- Set $GAM(IS,1) = CON(IS)$, $IS = 1, NSPEC$
- CALL NPWEIGHT (GAM,1,1,1,'mole/mole',WT) to get free-stream molecular weight WT(1).
- POST-SHOCK CONDITIONS
 - Set up initial shock geometry and free-stream conditions dependent on this geometry. In this hypothetical case, a uniform free stream is assumed.
 - Since the shock has infinitesimal thickness, there is no time for reactions to occur in a gas parcel crossing the shock. Therefore, set $GAM(IS,IP) = CON(IS)$ for $IS = 1, NSPEC$ and $IP = 1, NSH$ where NSH is the number of points immediately behind the shock.
 - CALL NP THERM (TFS,TFS,TFS,1,NSH,1,MODEL,HSF,HSF,HSF,CPS,CPS,CPS) where TFS is free-stream temperature and HSF is the corresponding species enthalpy.
 - Calculate $\Sigma GAM(IS,IP) * HSF(IS,IP)$ at each point on the shock to get the static enthalpy of the free-stream mixture.
 - From momentum and mass conservation, estimate a velocity and then a post-shock static enthalpy h . Also estimate a corresponding temperature T .
 - CALL NPHFINDT(h ,GAM,1,1,NSH,1,T) to get the post-shock temperature.
 - Change, say, the post-shock density and repeat the last two steps until convergence is obtained.
- INITIALIZE SHOCK LAYER
 - Estimate temperature T , pressure P , and mole-fraction distributions consistent with shock and surface conditions.
 - CALL NPWEIGHT to get the molecular weight and then calculate the density RO from the equation of state.
 - Save the mole fractions in CHI and CALL NP TO CON (GAM,NP,'mole/-mole',RO,WT) to convert GAM to concentration units.

- CALL NP THERM to get the enthalpy and specific heat distributions.
- CALL NP TRANS (LOW, NP, INC, T, T, CPS, CPS, CPS, GAM, D, VIS, EMU, TKT, TKT, TKT) to calculate the transport properties.
- Since an implicit algorithm will be employed by the flow solver, set DERIV = .TRUE.
- Since only air is involved, there will be virtually no low-temperature chemical activity, so to save computing time, set TMIN = 800.0.
- CALL NP SOURCE (GAM, T, DERIV, LOW, NP, INC, GAIN, LOSS, WDOT, DWDTM, DWDG).
- The user now has sufficient information to assign initial values to the variables at every point of the shock layer and also to initialize the integration algorithm.
- SOLVE CONSERVATION EQUATIONS
 - After the first pass, new values for global density, species concentrations, and mixture static enthalpy will be available at each point of the shock layer.
 - Call NP HFINDT to get the temperature at each point.
 - Call NP THERM to get species specific heats.
 - Call NP TRANS to reevaluate the transport properties.
 - Check magnitude of temperature and composition changes. If the changes are small enough, set DERIV = .FALSE. to save CPU time.
 - Call NP SOURCE to get new source terms.
 - Reapply solver until global convergence is obtained.
- REPORT RESULTS
 - Organize output data.
 - Call NP HFINDT to get final values for temperature T.

NOMENCLATURE

A_r	Constant in forward rate coefficient, Eq. (28), $m^3/kg\text{--mole}$ or $m^6/kg\text{--mole}^2$
$A_{i,j}$	Coefficient defined by Eq. (47), K^{1-i}
a_r	Effective activation temperature αC_r , Sec. 2.4.2, K
$a_{i,s}$	Thermo-fit coefficient, Eqs. (62) — (64), K^{1-i}
B_r	Constant in forward rate coefficient, Eq. (28)
$b_{i,s}$	Coefficient in viscosity fit, Eq. (65)
C_r	Activation temperature, Eq. (28), K
$C_{p,s}$	Constant pressure molar heat capacity of species s , $J/kg \text{ — mole}/K$
D_r	Constant in reverse rate coefficient, Eq. (67)
D_a	Ambipolar diffusion coefficient, m^2/s
D_s	Effective diffusion coefficient, Eq. (16), m^2/s
D_s^T	Thermal diffusion constant, m^{-1}
$\mathcal{D}_{i,j}$	Binary diffusion constant, m^2/s
d_s	Diffusion vector defined in Eq. (14)
$d_{k,i,s}$	Coefficient in Eq. (66)
\hat{E}	Total specific energy of mixture, J/kg
E_r	Constant in reverse rate coefficient, Eq. (67)
e	Magnitude of charge on electron, C
\hat{e}^l	Mixture internal energy of type l , J/kg

\hat{e}_s^l	Species internal energy of type, l , J/kg
F_r	Constant in reverse rate coefficient, Eq. (67)
ΔF	Change in free energy, $J/kg - mole$
\mathcal{F}_s^i	i th component of body force on species s , $N/kg - mole$
G_s^0	Gibbs free energy of species s , $J/kg - mole$
\mathcal{G}_s	Rate of appearance of species s , $kg - mole/m^3/s$
$\mathcal{G}_{r,s}$	Contribution of reaction r to \mathcal{G}_s , $kg - mole/m^3/s$
g_l	Degeneracy of electronic state l
g_r	Pseudo-temperature, Eq. (39)
\hat{H}	Total enthalpy of mixture, J/kg
\hat{h}_s	Mass-specific static enthalpy of species s , J/kg
h_s	Static enthalpy of species s , $J/kg - mole$
$h_{0,s}^0$	Heat of formation at 0 K and 1 atm pressure of species s , $J/kg - mole$
h_s^{lr}	Translation-rotation enthalpy of species s , $J/kg - mole$
h_s^V	Vibration-electronic enthalpy of species s , $J/kg - mole$
h_s^ν	Vibrational enthalpy of species s , $J/kg - mole$
h_s^e	Electronic enthalpy of species s , $J/kg - mole$
\mathcal{I}_s	Ionization energy of species s , Sec. 2.6, $J/kg - mole$
$J_{i,j}$	Element of Jacobian
K_r^c	Equilibrium constant, Eq. (30)

k_r^f	Forward rate coefficient of reaction r , $m^3/kg - mole$ or $m^6/kg - mole^2$
k_r^r	Reverse rate coefficient of reaction r , $m^3/kg - mole$ or $m^6/kg - mole^2$
L	Debye length, m
\mathcal{L}_s	Rate of disappearance of species s , $kg - mole/m^3/s$
$\mathcal{L}_{r,s}$	Contribution of reaction r to \mathcal{L}_s , $kg - mole/m^3/s$
M	A generic molecule, $kg - mole$
\mathcal{M}'_s	Molecular weight of species, $kg/kg - mole$
m_e	Electron mass, kg
\mathcal{N}	Avogadro's number
N_{LEV}	Number of electronic energy levels
N_r	Number of reactions
N_s	Number of species
n_e	Electron number density, m^{-3}
N_T	Number of temperature types
p	Static pressure of mixture, N/m^2
p_s	Partial pressure of species s , N/m^2
$\mathcal{P}_{i,j}$	Probability of vibrational energy exchange
Q	Radiant energy transfer rate, $J/m^2/s$
\bar{q}	Heat flux vector, $J/m^2/s$
\mathcal{R}	Universal gas constant, $J/kg - mole/K$

S	Electrostatic shielding ratio
S_e^{e-c}	Electron energy loss rate by impact ionization, $J/m^3/s$
S_e^{e-T}	Electron energy loss rate by collision, $J/m^3/s$
S_s^{v-c}	Vibration energy gain by chemical reaction, $J/m^3/s$
S_s^{v-v}	Vibration energy gain by exchange, $J/m^3/s$
S_s^{v-e}	Vibrational energy gained by electron impact for species s , W/m^3
S_s^{v-T}	Vibrational energy source for species s , W/m^3
$T_{d,s}$	Dissociation temperature of species s , K
T_q	Generic temperature, K
T_e	Translational temperature of free electrons, K
T_i	Generic internal temperature, K
T	Translational temperature, K
T_V	Temperature of all internal modes other than rotation, K
T_v	Vibrational temperature, K
T^*	Pseudo-temperature, Eq. (41), K
$T_{0,r}$	Pseudo-temperature, Eq. (40), K
t	Time, s
\mathcal{T}	Natural logarithm of T
U	Mass averaged flow velocity, m/s

U^i	i th component of U , m/s
u_s	Diffusion velocity of species s , m/s
u_s^i	i th component of u_s , m/s
v	Vibrational quantum number
\dot{w}_s	Rate of production of species s , $kg - mole/m^3/s$
Y_s	Mass fraction of species s
Z_{AB}	Vibrational partition function, Eq. (35)
Z	Electronic partition function
z	$e_{v,s}/(\mathcal{R}T_v)$
α	Coefficient defined by Ref. 10
$\alpha_{i,j}$	Number of atoms of element i in species j
β	Exponent of T_v in Park's average T_q , Sec. 2.4
$\bar{\beta}$	Factor in Eq. (34)
Γ	Total concentration, $kg - mole/m^3$
$\Gamma(z,x)$	Incomplete gamma function
γ_s	Species concentration, $kg - mole/m^3$
Δ_s	Dissociation energy of species s , $J/kg - mole$
δ_r	Change in number of moles across reaction r
$\delta_{i,j}$	Kronecker delta; $= 1$ if $i = j$, $= 0$ if $i \neq j$
ϵ_l	Energy of l th electronic state, $J/kg - mole$

η	Viscosity of mixture, Ns/m^2
θ_s	Characteristic vibrational temperature of species s , K
x	Boltzmann constant, $J/particle/K$
λ_s	Frozen thermal conductivity of species s , $J/m/s/K$
λ^l	Type- l thermal conductivity of mixture, $J/m/s/K$
Λ	Electrostatic shielding function
$\nu_{r,s}$	Stoichiometric coefficient of reactants in reaction r
$\nu'_{r,s}$	Stoichiometric coefficient of products of reaction r
ν_s	Characteristic vibrational frequency, s^{-1}
ρ	Density of mixture, kg/m^3
ρ_s	Density of species s , kg/m^3
τ_s	Vibrational relaxation time, Eq. (44), s
ϕ	Probability of dissociation, Eqs. (39) – (41)
χ_s	Mole fraction of species s
Ψ_f	Forward coupling factor, Sec. 2.4.2
Ψ_r	Reverse coupling factor, Sec. 2.4.2
ψ_l	Dimensionless energy of l th electronic level
$\dot{\omega}^l$	Rate of increase of internal energy of type l , $J/kg/s$
$\mu_{i,j}$	Reduced mass of collision partners i and j , kg
μ_s	Mobility of ion s , $m^2/s/volt$